

Fock exchange in the augmented spherical waves method and the optical band gap

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vorgelegt von
Dipl.-Math. Erika Bott
aus Aschaffenburg

Berichterstatter: Prof. Dr. P. C. Schmidt

Mitberichterstatter: Prof. Dr. K.-P. Dinse, Prof. Dr. J. Kübler

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*Wie es einen bösen und bitteren Eifer gibt,
der von Gott trennt und zur Hölle führt, so
gibt es auch einen guten Eifer, der von der
Sünde trennt und zum ewigen Leben führt.*

*Das ist der Eifer, den die Mönche in
glühender Liebe betätigen sollen: Sie sollen
einander in gegenseitiger Achtung
übertreffen. Sie sollen ihre leiblichen und
charakterlichen Schwächen in großer Geduld
aneinander ertragen. Sie sollen sich in
gegenseitigem Gehorsam zu überbieten
suchen. Keiner soll den eigenen Vorteil
suchen, sondern den des anderen. Sie sollen
einander selbstlos die brüderliche Liebe
erweisen. Gott sollen sie in Liebe fürchten.
Ihrem Abt seien sie in aufrichtiger und
demütiger Liebe zugetan. Sie sollen nichts
höher stellen als Christus, der uns alle zum
ewigen Leben führen möge.*

(Benediktusregel — 72. Kapitel)

ut in omnibus glorificetur Deus

(Regula Benedicti LVII,9)

1. Preface

This work is concerned with the problem of obtaining from theoretical electronic structure calculations band gap values which are similar to those derived from experiments.

In spite of the great variety of advances in theoretical electronic structure calculations which have been proposed during the past few decades, the band gap problem continues to be a topic of current research interest.

Although the optical transition can not be described by a simple one electron process but only "by the *quasiparticles* of many-body theory [...] it has often been assumed that the quasiparticle energy-band structure is similar to the band structure of [...] fictitious non-interacting electrons" (Ref. [1]) and one is interested in a reliable method of electronic band structure calculations which produces good band gap values, that is, where the optical transition can be approximated by the difference in occupied and unoccupied one particle (pseudo) states. It would be of great help in many areas of research if band gap values of materials could be obtained from theoretical calculations without the need to first synthesize and examine these substances experimentally.

In the last few years it was found that the use of the Fock exchange energy, the so-called exact exchange energy, in density functional theory might result in HOMO-LUMO energy differences which are much closer to the experimental band gaps than the Hartree-Fock or the usual density functional approach. This finding has only been verified by calculations for a few simple crystals like Si or MgO. The use of the Fock exchange instead of the usual local exchange leads to an increase in computer time by a factor in the order of 100. Therefore it is of interest to use the exact exchange method on the basis of a fast density functional band structure method. One example is the augmented spherical waves (ASW) method. However, one main reason for the efficiency of the ASW method is the use of the momentum analysis based on the electron density whereas in the new approach one has to use the Kohn-Sham orbitals themselves.

There are different ways to incorporate the exact exchange into the band structure procedure. The aim of the present work is to find an appropriate way to include the exact exchange into the ASW procedure and to find out how the omission of the momentum analysis affects the ASW computer program.

2. Introduction

This introduction presents an overview of the work contained in this thesis. The theoretical background is given in the appropriate sections.

In chapter 3 we present the fundamental terminology of band structure and explain why it is desirable to be able to calculate band gaps theoretically.

Chapter 4 presents background knowledge:

Section 4.1 is dedicated to the mathematical background necessary for a proper understanding of the remaining sections. In particular, the reader is made familiar with the requisite theory of functional derivation.

Section 4.2 is concerned with the historical development of density functional theory (DFT) which is a basic concept ubiquitous in the electronic structure calculation methods appearing in the course of this work.

The following section 4.3 then deals with the question if and how band gap values can be obtained from the outcome of electronic structure calculations.

Chapter 5 deals with the question which method obtains which results for the band gaps.

In section 5.1 we review a variety of methods for electronic structure calculations which have been or still are in use.

For the remainder of this work we then specialize on using the so-called exact exchange energy for the exchange-correlation energy functional which is part of the total energy functional. We explain the reasons for this choice in section 5.2.

In section 5.3 we highlight the difficulties in the evaluation of the exact exchange potential, the potential function corresponding to the exact exchange energy, and in section 5.4 we discuss how to overcome these difficulties.

Already in the course of section 5.4 we meet the approximation of Krieger, Li, and Iafrate for the exact exchange on which the Krieger-Li-Iafrate (KLI) method is based. This KLI method is then introduced in detail in section 6.1.

Sections 6.2 and 6.3 present some of the properties of the KLI method which make it a very promising scheme.

In the subsequent sections 6.4 and 6.5 we adapt the central KLI formulas to a program for atomic calculations and to the augmented spherical waves (ASW) program for solids, respectively.

Finally, section 6.6 is dedicated to the question of how the computational expenditure in performing the KLI formalism can be reduced when some equal Kohn-Sham orbitals occur.

Chapter 7 then deals with the so-called exact Slater approach.

It starts with our derivation in section 7.1 of a simpler but apparently inferior approximation to the exact exchange potential than that given by KLI. We recognize this to be identical with the exact Slater exchange potential; however, we arrive at it in a different way than Slater.

Sections 7.2 and 7.3 then deal with the adaption of the exact Slater exchange potential to the program for atomic calculations and to the augmented spherical waves (ASW) program for solids, respectively.

In Chapter 8 a comparison of the KLI exchange potential with the exact Slater exchange potential in the case of atomic calculations and of rare gas solids is made.

The work is concluded by conclusions (in German) and by an appendix.

3. Band gaps and optical transitions

We are not going to explain in this work the concepts of reciprocal space and of the energy bands for solids defined therein.

If you want to know more about these fundamentals of solid state physics, a standard textbook is recommended, e.g., Ref. [2]. A brief account of these basics can also be found in sections 2–4 of Ref. [3].

For now let us recall the terms "valence bands" and "conduction bands" which occur in the context of semiconductors and insulators and label the highest occupied energy bands and the lowest unoccupied energy bands, respectively. Hereby the characteristic feature of semiconductors and insulators is the fact that the conduction band minimum is higher in energy than the valence band maximum by some nonvanishing positive number E_g , the so-called band gap or optical energy gap. In contrast, in a metal there exists at least one partially filled energy band and no energy gap between occupied and unoccupied states occurs (compare Fig. 3.1).

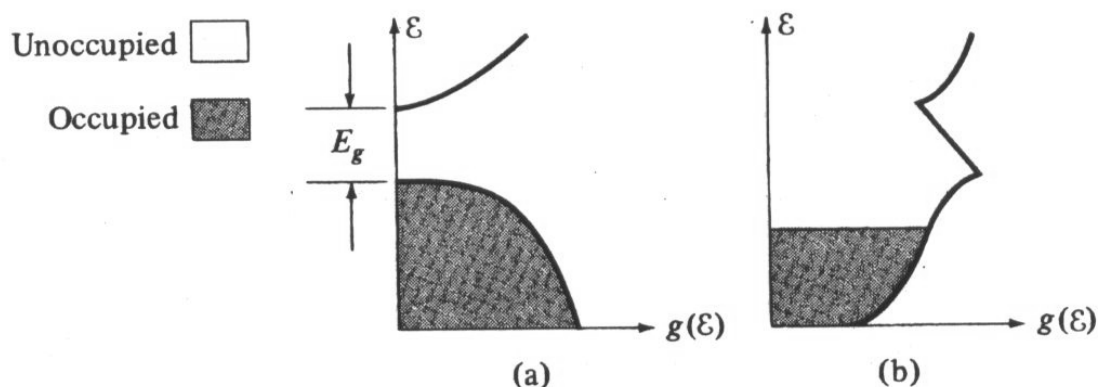


Fig. 3.1: (from Ref. [2], p. 562) Schematic plot of the density of levels (horizontally) vs. energy (vertically) for an insulator (a) and a metal (b). (a) In an insulator there is a region of forbidden energies separating the highest occupied and lowest unoccupied levels. (b) In a metal the boundary occurs in a region of allowed levels.

Basically, two types of band gaps can occur, namely the direct band gaps where the valence band maximum and the conduction band minimum are at the same point in reciprocal space (Fig. 3.2(a)), and the indirect band gaps where the valence band maximum and the conduction band minimum are at different points in reciprocal space (Fig. 3.2(b)).

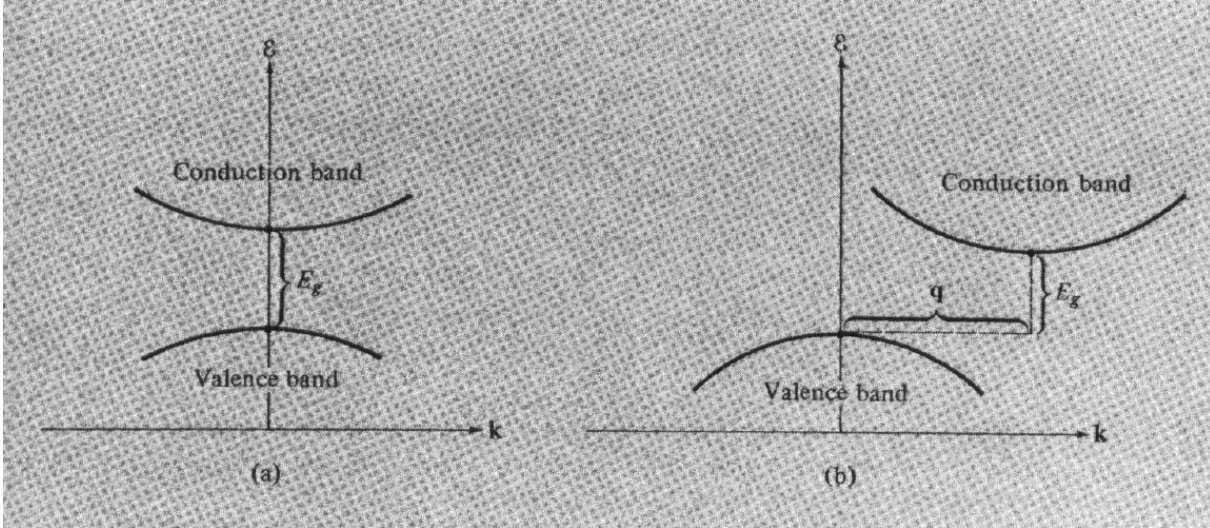


Fig. 3.2: (from Ref. [2], p. 567) Schematic plot of energy band diagrams with (a) a direct band gap and (b) an indirect band gap.

A very nice example for a substance with an indirect band gap is silicon which has an indirect band gap of width 1.1 eV (see Fig. 3.3).

An important phenomenon in the context of band gaps is the fact that impurities introduced into a substance with a band gap can lead to additional energy levels in the energy gap range of the pure substance (see Fig. 3.4) which influence the optical properties drastically.

Considering for example a fluorescent material it is desirable that the emission frequency ν corresponds to the difference between two calculated one electron states $\epsilon_j - \epsilon_i = h\nu$ or to the calculated band gap $E_g = h\nu$.

As we will point out in the next sections this correlation is usually not fulfilled. For example in the Hartree-Fock method the experimental band edge transitions are lower in energy than the calculated ones. The opposite holds for the usual density functional method. As an example we show calculated band structures for Ar obtained in the Hartree-Fock (HF) method (Fig. 3.5) and in the usual density functional method (local spin density, LSD, Fig. 3.6). Fig. 3.5 is taken from p. 645 of Ref. [4] with energies given in Rydberg and Fig. 3.6 is taken from p. 6000 of Ref. [5] with energies given in eV. The obtained band gaps are 18.52 eV in the HF method and 7.9 eV in the LSD method; the experimental band gap is 14.16 eV (see Ref. [6]).

Provided we have a calculation method producing experimental band gap values, it is much easier than now to analyse the microscopic process of the electronic transitions in order to support the development of new luminescent materials.

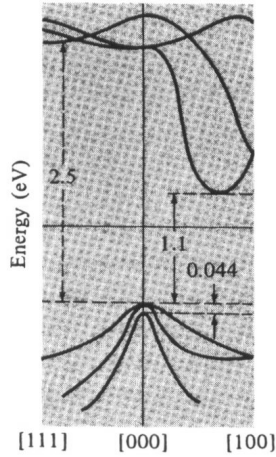


Fig. 3.3: (from Ref. [2], p. 569) Energy bands in silicon. Silicon has an indirect band gap since the valence band maximum occurs at the origin of reciprocal space whereas the conduction band minima lie in reciprocal space some distance away along the $\langle 100 \rangle$ directions.

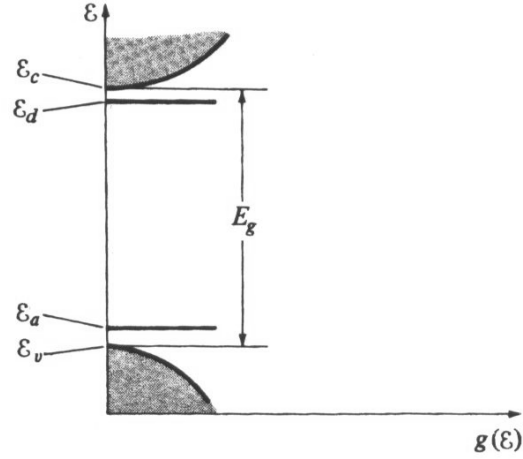


Fig. 3.4: (from Ref. [2], p. 579) Level density for a semiconductor containing both donor and acceptor impurities. The donor levels, ε_d , are generally close to the bottom of the conduction band, ε_c , compared with E_g , and the acceptor levels, ε_a , are generally close to the top of the valence band, ε_v .

But of course luminescence is only one field where band gaps play an important role. Another one is the large field of conductivity phenomena.

The great importance of band gaps and of the size of band gaps becomes quite apparent from the large number of publications which are concerned with band gaps and with band gap related issues, e.g., Refs. [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22].

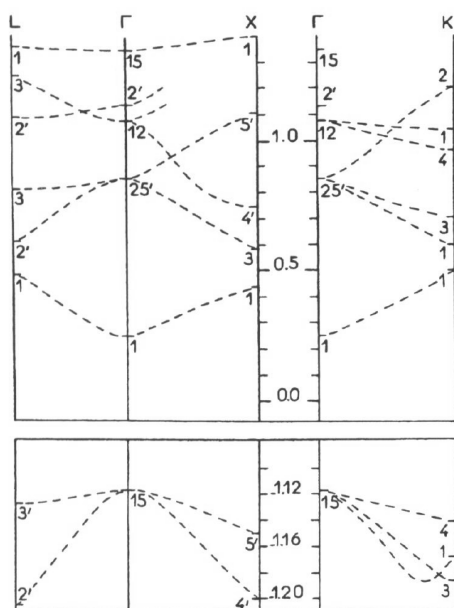


Fig. 3.5: (from Ref. [4], p. 645) Argon HF band structure, energies in Rydberg. Note the change in scale between the valence and conduction bands. The calculated band gap is 18.52 eV.

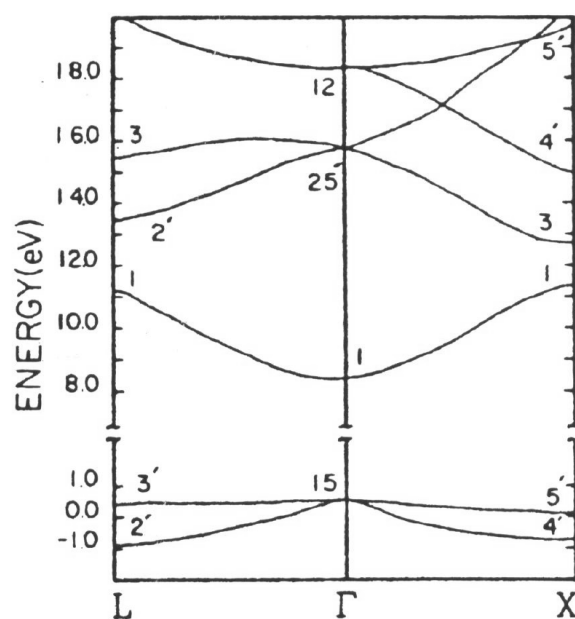


Fig. 3.6: (from Ref. [5], p. 6000) Argon LSD band structure, energies in eV. The calculated band gap is 7.9 eV.

4. Background knowledge

4.1 Aspects of functional derivation

If you are interested in a genuinely mathematical presentation of differential calculus and functional derivation, I recommend section 0.2. *Differential calculus* in Ref. [23].

However, since we will only need very special functionals in the following sections, namely functionals

$$F : U \rightarrow \mathcal{C} \quad (4.1)$$

$$\text{or } G : U \rightarrow \mathcal{L}_2(\mathcal{R}^3) \quad (4.2)$$

where U is a subspace of the linear space $\mathcal{L}_2(\mathcal{R}^3)$ of all square-integrable functions

$$f : \mathcal{R}^3 \rightarrow \mathcal{C} \quad (4.3)$$

defined in real space and where \mathcal{C} denotes the complex numbers, we will in the following restrict our attention to the functional derivation of such functionals.

Furthermore, as scalar product on the linear space $\mathcal{L}_2(\mathcal{R}^3)$ of all square-integrable functions $f : \mathcal{R}^3 \rightarrow \mathcal{C}$ we use

$$\langle f, g \rangle := \int f(\mathbf{r})^* g(\mathbf{r}) d\mathbf{r} \quad (4.4)$$

and consequently, the norm on $\mathcal{L}_2(\mathcal{R}^3)$ is given by

$$\|f\| := \sqrt{\langle f, f \rangle} = \sqrt{\int |f(\mathbf{r})|^2 d\mathbf{r}}. \quad (4.5)$$

Now, the functional derivative $\frac{\delta F[f]}{\delta f(\mathbf{r})}$ of $F[f]$ with respect to f — where $F : U \rightarrow \mathcal{C}, U \subset \mathcal{L}_2(\mathcal{R}^3)$ — is by definition a function in $\mathcal{L}_2(\mathcal{R}^3)$ such that

$$F[f + h] - F[f] = \left\langle \frac{\delta F[f]}{\delta f(\mathbf{r})}, h \right\rangle + o(\|h\|) \quad (4.6)$$

for any $h \in \mathcal{L}_2(\mathcal{R}^3)$ where

$$\lim_{\|h\| \rightarrow 0} \frac{o(\|h\|)}{\|h\|} = 0. \quad (4.7)$$

Using our special scalar product this simply means that $\frac{\delta F[f]}{\delta f(\mathbf{r})}$ is such that

$$F[f + h] - F[f] = \int \left(\frac{\delta F[f]}{\delta f(\mathbf{r})} \right)^* h(\mathbf{r}) d\mathbf{r} + o(\|h\|) \quad \text{for all } h \in \mathcal{L}_2(\mathcal{R}^3) \quad (4.8)$$

where $\lim_{\|h\| \rightarrow 0} \frac{o(\|h\|)}{\|h\|} = 0$.

For our purposes, $\frac{\delta F[f]}{\delta f(\mathbf{r})}$ is uniquely determined by the condition (4.8) — more precisely, two functions fulfilling the condition (4.8) differ only on a subset V of \mathcal{R}^3 with zero Lebesgue measure (cf. Proposition 1 of section 0.2. in Ref. [23]).

Similarly, for $G : U \rightarrow \mathcal{L}_2(\mathcal{R}^3)$, $U \subset \mathcal{L}_2(\mathcal{R}^3)$, the derivative $\frac{\delta G[f](\mathbf{r})}{\delta f(\mathbf{r})}$ is defined by

$$(G[f + h] - G[f])(\mathbf{r}) = \int \left(\frac{\delta G[f](\mathbf{r})}{\delta f(\mathbf{r}')} \right)^* h(\mathbf{r}') d\mathbf{r}' + s[h](\mathbf{r}) \quad (4.9)$$

for any $h \in \mathcal{L}_2(\mathcal{R}^3)$ where

$$\lim_{\|h\| \rightarrow 0} \frac{\|s[h]\|}{\|h\|} = 0. \quad (4.10)$$

When G is such that it maps functions f on, say, functions g , we shall often simply write

$$\frac{\delta g(\mathbf{r})}{\delta f(\mathbf{r}')} \quad \text{instead of} \quad \frac{\delta G[f](\mathbf{r})}{\delta f(\mathbf{r}')}. \quad (4.11)$$

For our purposes, the chain rule for functional derivatives (cf. section 0.2.3. in Ref. [23]) will be very important.

For us, this chain rule implies that when the functional context is such that functions g are mapped to functions h and the functions h are mapped to numbers $F[g]$, then

$$\frac{\delta F[g]}{\delta g(\mathbf{r})} = \int \frac{\delta F[g]}{\delta h(\mathbf{r}')} \cdot \frac{\delta h(\mathbf{r}')}{\delta g(\mathbf{r})} d\mathbf{r}'; \quad (4.12)$$

when the functional context is such that functions g are mapped to functions h and the functions h are mapped to functions f , then

$$\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r}')} = \int \frac{\delta f(\mathbf{r})}{\delta h(\mathbf{r}'')} \cdot \frac{\delta h(\mathbf{r}'')}{\delta g(\mathbf{r}')} d\mathbf{r}'' . \quad (4.13)$$

To make this form of the chain rule plausible, we briefly try to see that the relationship (4.13) makes sense whereby in this little part, by \approx we denote equality to first order, i.e., we neglect " $s[h]$ terms".

For $\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r}')}$ we have the condition

$$(f[g + \Delta g] - f[g])(\mathbf{r}) \approx \int \left(\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r}')} \right)^* \Delta g(\mathbf{r}') d\mathbf{r}'. \quad (4.14)$$

In the right hand side of this equation, substituting $\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r})}$ by the right hand side of (4.13) we find

$$\begin{aligned}
& \int \left(\int \frac{\delta f(\mathbf{r})}{\delta h(\mathbf{r}'')} \cdot \frac{\delta h(\mathbf{r}'')}{\delta g(\mathbf{r}')} d\mathbf{r}'' \right)^* \Delta g(\mathbf{r}') d\mathbf{r}' \\
&= \int \left(\frac{\delta f(\mathbf{r})}{\delta h(\mathbf{r}'')} \right)^* \int \left(\frac{\delta h(\mathbf{r}'')}{\delta g(\mathbf{r}')} \right)^* \Delta g(\mathbf{r}') d\mathbf{r}' d\mathbf{r}'' \\
&\approx \int \left(\frac{\delta f(\mathbf{r})}{\delta h(\mathbf{r}'')} \right)^* (h[g + \Delta g] - h[g])(\mathbf{r}'') d\mathbf{r}'' \\
&\approx (f[g + \Delta g] - f[g])(\mathbf{r}),
\end{aligned} \tag{4.15}$$

just as we wanted.

That the relationship (4.12) makes sense, can be seen in a similar way.

More generally, when functions g are mapped to sets of functions h_i ($i = 1, \dots, N$) which determine the values $F[g]$ and the functions f , respectively, the chain rules read

$$\frac{\delta F[g]}{\delta g(\mathbf{r})} = \sum_{i=1}^N \int \frac{\delta F[g]}{\delta h_i(\mathbf{r}')} \frac{\delta h_i(\mathbf{r}')}{\delta g(\mathbf{r})} d\mathbf{r}' \tag{4.16}$$

and

$$\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r}')} = \sum_{i=1}^N \int \frac{\delta f(\mathbf{r})}{\delta h_i(\mathbf{r}'')} \frac{\delta h_i(\mathbf{r}'')}{\delta g(\mathbf{r}')} d\mathbf{r}'', \tag{4.17}$$

respectively.

4.2 Some basic concepts of density functional theory (DFT)

In this section we briefly discuss what is meant by "density functional theory" (DFT).

As is well known, the many-electron wave function of a system, from which all other observables can be obtained, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, is the solution of Schrödinger's equation of quantum mechanics,

$$\hat{H}\Psi = E\Psi, \quad (4.18)$$

where $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ are the coordinates of the N electrons of the system. \hat{H} is the energy operator, the so-called hamiltonian, of the system and E is the total energy of the system. \hat{H} consists of a kinetic energy part \hat{T} and a potential energy part \hat{V} , i.e.,

$$\hat{H} = \hat{T} + \hat{V}. \quad (4.19)$$

It is also well known, however, that Schrödinger's equation becomes highly demanding already for moderately large systems like even rather small atoms and that accurate analytical solutions can be found in very simple cases only, like, for example, in the case of the hydrogen atom.

For systems with few electrons it is possible to determine in principle the exact wave function by the "configuration interaction" (CI) method; nevertheless, both the problems to be solved and the interpretation of the results of the CI method become too difficult already for moderately large systems.

Therefore scientists have for decades been trying to find approximate solutions to the many-particle problem from which the important properties of the systems in question can be deduced to high accuracy.

One of the first approximations which is very famous indeed is due to Hartree [24]. He approximated the many-electron wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ by a product of normalized one-electron wave functions:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \cdot \dots \cdot \psi_N(\mathbf{r}_N). \quad (4.20)$$

He then varied these one-electron wave functions $\psi_1(\mathbf{r}_1), \dots, \psi_N(\mathbf{r}_N)$ such that the total energy

$$\begin{aligned} E &= \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{H} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= \int \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) \hat{H} \psi_1(\mathbf{r}_1) \dots \psi_N(\mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \end{aligned} \quad (4.21)$$

assumes its minimum.

The Hartree-Fock approach [25] is similar. There the many-electron wave function is approximated by a Slater determinant,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_1(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (4.22)$$

and consequently the Hartree-Fock equations are obtained by varying the functions ψ_i such that the total energy

$$E = \frac{1}{n!} \int \begin{vmatrix} \psi_1^*(\mathbf{r}_1) & \dots & \psi_1^*(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_N^*(\mathbf{r}_1) & \dots & \psi_N^*(\mathbf{r}_N) \end{vmatrix} \hat{H} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_1(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix} d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (4.23)$$

assumes its minimum.

Now and for all that follows adopting atomic units, the resulting Hartree-Fock equations can be written in two equivalent ways (cf. Ref. [26]):

$$\begin{aligned} \hat{H}_1 \psi_i(\mathbf{r}_1) + \left[\sum_{k=1}^N \int \frac{\psi_k^*(\mathbf{r}_2) \psi_k(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1) - \sum_{k=1}^N \left[\int \frac{\psi_k^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_k(\mathbf{r}_1) &= \varepsilon_i \psi_i(\mathbf{r}_1), \\ i &= 1, \dots, N \end{aligned} \quad (4.24)$$

and

$$\begin{aligned} \hat{H}_1 \psi_i(\mathbf{r}_1) + \left[\sum_{k=1}^N \int \frac{\psi_k^*(\mathbf{r}_2) \psi_k(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1) & \\ - \left[\sum_{k=1}^N \frac{1}{\psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_1)} \int \frac{\psi_i^*(\mathbf{r}_1) \psi_k^*(\mathbf{r}_2) \psi_k(\mathbf{r}_1) \psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1) &= \varepsilon_i \psi_i(\mathbf{r}_1), \\ i &= 1, \dots, N. \end{aligned} \quad (4.25)$$

Here

$$\hat{H}_1 = -\frac{1}{2} \nabla^2 + V_n(\mathbf{r}_1) \quad (4.26)$$

is the kinetic energy operator for the electron of coordinates \mathbf{r}_1 plus V_n , the external field due to the nuclei acting on the electrons.

The second terms,

$$\left[\sum_{k=1}^N \int \frac{\psi_k^*(\mathbf{r}_2) \psi_k(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1), \quad (4.27)$$

are the Coulomb contributions due to the interaction of electrons at \mathbf{r}_1 and \mathbf{r}_2 .

Finally, the last terms on the left hand sides are the so-called exchange terms and the values ε_i are the single-particle eigenvalues which do not have an immediate physical meaning.

These approximations were in use long before the concept of density functional theory was born.

The central feature of DFT is its focus on the electron density $n(\mathbf{r})$ of a system,

$$n(\mathbf{r}) = N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (4.28)$$

rather than its wave function Ψ .

A first step in this direction was taken by Thomas [27] and Fermi [28] who proposed a formula for the calculation of the kinetic energy of a system from its electron density $n(\mathbf{r})$ which was based on the results obtained for free electrons.

The great foundation of DFT is the assertion that any observable of a static many-particle system is uniquely determined by the ground state electron density $n(\mathbf{r})$ of this system. This is an implication of the famous Hohenberg-Kohn theorem [29] and is usually stated by saying that any observable of a static many-particle system is a functional of the ground state electron density $n(\mathbf{r})$ of this system. This means that to any observable of such a system there exists a functional F mapping the electron densities to the observables such that $F[n]$ is the requested observable for the system with ground state density $n(\mathbf{r})$.

Unfortunately the exact form of most of these functionals is unknown — and many of them will not have a nice and easy form.

However, one can always try with approximations. The Hohenberg-Kohn theorem also makes sure that for a physical system with some given external potential $v_0(\mathbf{r})$ the energy functional $E_{v_0}[n]$ assumes its minimum value

$$E_0 = E_{v_0}[n_0] \quad (4.29)$$

when the correct ground state electron density $n_0(\mathbf{r})$ of the system is used; for all other electron densities $n(\mathbf{r})$ one has

$$E_0 < E_{v_0}[n]. \quad (4.30)$$

This made scientists try to determine the ground state electron density of a system by constructing approximate energy functionals $E[n]$ and minimizing them with respect to the electron density. Unfortunately, in particular the approximations to the kinetic part of the energy functional by functionals depending explicitly on the electron density $n(\mathbf{r})$ turned out to be very poor and therefore one did not achieve satisfactory results.

A possible way out of this dilemma was found by Kohn and Sham [30] who showed that it is not necessary to use the electron density $n(\mathbf{r})$ as the only variable function but that one can use an intermediary orbital picture.

Their work finally led to the Kohn-Sham theorem and to the Kohn-Sham scheme which has since been found to be very successful and is also the basis of the electronic structure calculation methods used by us. We now outline the basics of the Kohn-Sham theorem and -scheme.

Starting point is the use of an auxiliary system of N non-interacting particles with corresponding wave functions $\varphi_i(\mathbf{r}), i = 1, \dots, N$, which are also called Kohn-Sham orbitals. This auxiliary system has the hamiltonian

$$\hat{H}_s = \hat{T}_s + V_s \quad (4.31)$$

and, as before, to any such hamiltonian there exists some electron density $n_s(\mathbf{r})$ minimizing the corresponding energy functional

$$\begin{aligned} E_s[n] &= T_s[n] + \int v_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = \sum_{i=1}^N \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_i(\mathbf{r}) d\mathbf{r} + \int v_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \\ n(\mathbf{r}) &= \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2. \end{aligned} \quad (4.32)$$

The Kohn-Sham theorem makes sure that to an interacting system with external potential $v_0(\mathbf{r})$ there exists some "effective potential" $v_s(\mathbf{r})$ such that the ground state electron density $n_s(\mathbf{r})$ of the non-interacting system with potential function $v_s(\mathbf{r})$ is equal to the ground state electron density $n_0(\mathbf{r})$ of the interacting system with external potential $v_0(\mathbf{r})$.

Once $v_s(\mathbf{r})$ is known, one can then of course obtain the electron density $n_0(\mathbf{r})$ from the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ as

$$n_0(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (4.33)$$

where the $\varphi_i(\mathbf{r})$ can be calculated by solving Schrödinger's equation

$$\left(-\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), i = 1, \dots, N. \quad (4.34)$$

We should therefore try and express $v_s(\mathbf{r})$ in terms of the known $v_0(\mathbf{r})$. To do this, we rewrite the total energy functional $E_{v_0}[n]$ as

$$E_{v_0}[n] = T_s[n] + \int v_0(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] \quad (4.35)$$

where the so-called exchange-correlation energy $E_{xc}[n]$ is simply what is needed to make Eq. (4.35) a true equality. In fact, $E_{xc}[n]$ is the part of $E_{v_0}[n]$ which is not known explicitly and has to be approximated.

As is shown in section 4.1 of Ref. [31], for $v_{s,0}(\mathbf{r})$, the effective potential corresponding to the ground state electron density $n_0(\mathbf{r})$, one obtains an expression that one might expect from Eq. (4.35):

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}([n_0]; \mathbf{r}) \quad (4.36)$$

where

$$v_{xc}([n_0]; \mathbf{r}) := \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n=n_0} \quad (4.37)$$

denotes the exchange-correlation potential.

Now we are sufficiently prepared to face the Kohn-Sham scheme which is nicely presented in section 4.2 of Ref. [31]:

The exact ground state density $n(\mathbf{r})$ of an interacting system with external potential $v_0(\mathbf{r})$ can be obtained by self-consistent solution of the following set of equations

$$\left(-\frac{1}{2} \nabla^2 + v_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}([n]; \mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots \quad (4.38)$$

with

$$n(\mathbf{r}) = \sum_{i=1}^{\infty} \gamma_i |\varphi_i(\mathbf{r})|^2 \quad (4.39)$$

and occupation numbers γ_i satisfying

$$\gamma_i = 1 \quad : \quad \varepsilon_i < \mu \quad (4.40)$$

$$0 \leq \gamma_i \leq 1 \quad : \quad \varepsilon_i = \mu \quad (4.41)$$

$$\gamma_i = 0 \quad : \quad \varepsilon_i > \mu \quad (4.42)$$

and

$$\sum_{i=1}^{\infty} \gamma_i = N \quad (4.43)$$

for suitable μ .

The exchange-correlation potential $v_{xc}(\mathbf{r}) := v_{xc}([n]; \mathbf{r})$ is defined as

$$v_{xc}(\mathbf{r}) := v_{xc}([n]; \mathbf{r}) := \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (4.44)$$

By solving the above system (4.38)–(4.43) self-consistently we mean basically the following:

We start with some guess $n^{(0)}(\mathbf{r})$ for the electron density, solve the Schrödinger equations (4.38), construct from the resulting Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ and (4.39)–(4.43) a new electron density $n^{(1)}(\mathbf{r})$, plug this $n^{(1)}(\mathbf{r})$ into (4.38) to calculate new Kohn-Sham orbitals and from these another new density $n^{(2)}(\mathbf{r})$, and so on. This process is in principle iterated until the densities $n^{(j)}(\mathbf{r})$ no longer change from one step to the next: the system is now self-consistent in that we have found a density $n_0(\mathbf{r})$ which, on being substituted into (4.38), leads to itself as result when (4.38)–(4.43) is solved. This $n_0(\mathbf{r})$ is by the Kohn-Sham theorem our wanted ground state density.

The great issue that is left to research is the question of how $E_{xc}[n]$ or $v_{xc}([n]; \mathbf{r})$ should be chosen. This is also the central issue of most of the remaining sections of this work.

A point I want to make clear before we close the present section is that it is legal to express $E_{xc}[n]$ and $v_{xc}([n]; \mathbf{r})$ as explicit functionals of the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$:

The self-consistent system (4.38)–(4.43) provides a bijection between ground state electron densities $n(\mathbf{r})$ and the corresponding Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ since Eq. (4.38) allows the calculation of the $\varphi_i(\mathbf{r})$ from $n(\mathbf{r})$ and (4.39)–(4.43) allows the calculation of $n(\mathbf{r})$ from the $\varphi_i(\mathbf{r})$.

Hence the Kohn-Sham orbitals are functionals of the electron density $n(\mathbf{r})$:

$$\varphi_i(\mathbf{r}) = \varphi_i([n]; \mathbf{r}) \quad (4.45)$$

and consequently any functional of the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ is naturally also a functional of the electron density $n(\mathbf{r})$.

Now, since we do not really have any precise information about the form of the functionals $E_{xc}[n]$ and $v_{xc}([n]; \mathbf{r})$, we may use for them any suitable expression as long as it is a functional of the electron density $n(\mathbf{r})$. Of course, we would be particularly glad if we could give some plausible justification for the choices we make.

4.3 How are band gaps obtained from the results of electronic structure calculations?

In section 4.2 we saw that by applying the Kohn-Sham scheme to a given physical system characterized by its external potential $v_0(\mathbf{r})$ we obtain the following immediate results:

$$n(\mathbf{r}), \text{ the ground state electron density,} \quad (4.46)$$

$$\varphi_i(\mathbf{r}), \text{ the Kohn - Sham orbitals,} \quad (4.47)$$

$$\varepsilon_i (\varepsilon_1 \leq \varepsilon_2 \leq \dots), \text{ the one - particle eigenvalues.} \quad (4.48)$$

Furthermore, from Eq. (4.35) we can then calculate the total ground state energy $E_{v_0}[n]$ of the given system.

For the following we keep the external potential $v_0(\mathbf{r})$ of the system in consideration fixed. We then denote the total ground state energy $E_{v_0}[n]$ of an N -particle system with this external potential as $E(N)$ and its one-particle Kohn-Sham eigenvalues ε_i as $\varepsilon_i(N)$ ($\varepsilon_1(N) \leq \varepsilon_2(N) \leq \dots$).

If the physical system in consideration now is a semiconductor or insulator with N electrons, the principal band gap E_g is given by differences of ground state energies of N and $N \pm 1$ particle systems [32]:

$$\begin{aligned} E_g &= (E(N+1) - E(N)) - (E(N) - E(N-1)) \\ &= E(N+1) + E(N-1) - 2E(N). \end{aligned} \quad (4.49)$$

However, from a numerical point of view it is not advisable to calculate band gaps from the formula Eq. (4.49) since this involves differences of large numbers which differ only to a small extent.

Luckily, even though the Kohn-Sham one-particle eigenvalues $\varepsilon_i(j)$ in general do not have any physical meaning — only $\varepsilon_j(j)$ can be interpreted as a physical electron removal energy — [33, 34], the band gap E_g can alternatively be expressed entirely in terms of KS eigenvalues [32]:

$$E_g = \varepsilon_{N+1}(N+1) - \varepsilon_N(N) \quad (4.50)$$

$$\begin{aligned} &= (\varepsilon_{N+1}(N) - \varepsilon_N(N)) + (\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)) \\ &= \varepsilon_g + \Delta_{xc} \end{aligned} \quad (4.51)$$

with

$$\varepsilon_g = \varepsilon_{N+1}(N) - \varepsilon_N(N) \quad (4.52)$$

$$\Delta_{xc} = \varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N). \quad (4.53)$$

It is consequently possible to calculate the band gap by forming the difference $\varepsilon_{N+1}(N+1) - \varepsilon_N(N)$ between the highest occupied one-particle eigenvalues from two Kohn-Sham calculations with $N+1$ and N particles, respectively (see Eq. (4.50)).

Alternatively, you can carry out a single Kohn-Sham calculation with N particles to obtain $\varepsilon_g = \varepsilon_{N+1}(N) - \varepsilon_N(N)$, the difference between the Kohn-Sham eigenvalues of the lowest unoccupied orbital and the highest occupied one; but then you have to take into account that you make a certain mistake Δ_{xc} (see Eq. (4.51)).

In fact, the contribution Δ_{xc} to the band gap arises from a finite discontinuity of the exchange-correlation potential $v_{xc}(\mathbf{r})$ at integer particle numbers.

To understand this notion, one first has to extend the Hohenberg-Kohn theorem and the Kohn-Sham scheme to fractional particle numbers N by using the concept of a statistical mixture. Then the curve of lowest average energy E_N versus N is found to be a series of straight line segments with slope discontinuities at integral N . As N increases through an integer M , the highest occupied Kohn-Sham orbital eigenvalue jumps from $E_M - E_{M-1}$ to $E_{M+1} - E_M$ and the exchange-correlation potential $v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$ jumps by the same constant (cf. Ref. [35]).

The discussion on the topic of the band gap correction term

$$\Delta_{xc} = E_g - \varepsilon_g \quad (4.54)$$

and its connection with the related derivative discontinuity of the exchange-correlation energy E_{xc} was started mainly by Perdew and Levy [36] and Sham and Schlüter [37].

Since then there has been quite a dispute going on about the derivative discontinuity of E_{xc} , about the magnitude and the importance of the correction term Δ_{xc} for the band gap values and about how Δ_{xc} could be incorporated into electronic structure calculation schemes.

We need not go into these details here and refer the reader interested in this particular topic to the numerous literature [1, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60].

5. Choice of an adequate method

5.1 Methods for electronic structure calculations and resulting optical band gaps

In this section we comment upon the quality of some methods for electronic structure calculations; hereby we are in particular interested in the accuracy with which they predict band gap values.

Historically one of the first methods was provided by the Hartree-Fock (HF) theory which we already introduced in section 4.2. However, this method is not suitable for some solid-state and molecular applications [61] since it produces unrealistic features in the HF energy eigenvalues, e.g., vanishing density of states at the Fermi level in metals [2] and unphysically large band gaps in insulators (sometimes by a factor 2–5) [62]. Furthermore for crystal HF calculations one needs large amounts of computer time.

Solid state calculations are mostly based on density functional theory (cf. section 4.2) and make use of the local density approximation (LDA) or its spin-dependent form, the local-spin-density (LSD) approximation to the exchange-correlation energy [29, 30, 63, 64].

In these approximations the exchange-correlation energy functional of the electron density or of the spin-density is chosen as an explicit functional of the density such that it has the correct form in the limiting cases of slowly varying density and of high density; in these limiting cases the correct exchange-correlation energy functional is known from the theory of the homogeneous electron gas [65]. Besides providing rather successful approximations for a wide range of physical quantities, Refs. [66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79], DFT with LDA or LSD is also fairly simple from a numerical point of view.

Nevertheless, some notable failures of this method have been encountered, Refs. [80, 81, 82, 83, 84]; in particular, band gaps are systematically underestimated by as much as 40%, as is well known, e.g., Refs. [1, 6, 32, 61, 85, 86, 87, 88, 89, 90].

Improved band gap values are for example obtained from the GW method of Hedin [91] which uses the concept of quasiparticle energies and perturbation theory. It is applied, e.g., in Refs. [47, 92, 93, 94]. However, the GW procedure does not allow one to calculate structural properties together with energy gaps in a self-consistent way [32].

An attempt to use a better approximation to the exchange-correlation energy than that provided by LDA/LSD is made by using generalized gradient approximations (GGA), Refs. [95, 96, 97, 98], which use functionals depending explicitly on both the electron density and its gradient.

It turns out, however, that the underestimate of the LDA band gaps is usually not improved by the GGA's [99].

A large field of alternative realizations of DFT other than LDA is opened by the concept of generalized Kohn-Sham (GKS) schemes [32].

An example for such a GKS scheme is provided by an approach for $v_{xc} = v_x + v_c$ with screened nonlocal exchange v_x and LDA correlation v_c potentials [50]; this "sX-LDA" method leads to band gaps far better than those of LDA [32].

Finally, there is a particular concept which has turned out to give much improved band gap values and which is used in a large variety of modifications, namely the self-interaction correction (SIC) method, Refs. [5, 61, 90, 100, 101, 102, 103, 104, 105, 106].

A special product of the SIC approach is the so-called exact exchange (EXX) energy term [107, 108, 109] which is widely used as an approximation for the exchange energy functional $E_x[n]$ ($E_{xc} = E_x + E_c$).

This is often done in conjunction with the optimized effective potential (OEP) method [103, 107, 110] or with a very good approximation to the OEP method, namely the Krieger-Li-Iafrate (KLI) method [51, 54, 90].

We will say more about SIC, EXX, OEP, and KLI in the subsequent sections.

5.2 Self-interaction corrections (SIC) and exact exchange

We open this section with a quotation from Ref. [1]:

”Electronic *excitations* are not, in general, described by DFT, but by the *quasi-particles* of many-body theory, whose energy $E(\mathbf{k})$ (the ”energy-band structure”) is the energy required to add an electron with given momentum to the system. Because of the absence of other techniques, it has often been assumed that the quasiparticle energy-band structure is similar to the band structure of the fictitious noninteracting electrons that appear in DFT, $E_{\text{DFT}}(\mathbf{k})$. This has been justified by the formal similarity of the Schrödinger-type equations that the DFT electrons and the quasiparticles obey, and by the exact result that at zero temperature, the Fermi energy, E_{F} is given correctly by the highest occupied DFT eigenvalue.”

This statement makes it clear that whenever an electronic structure calculation method based on DFT leads to good results for physical quantities like, e.g., band gap values, this has to be regarded as a lucky coincidence in the first place.

Nevertheless, scientists have by now agreed that the exchange-correlation potential v_{xc} should be endowed with some essential properties [111] by which one can be guided in the choice of the exchange-correlation energy functional $E_{\text{xc}}[n]$.

Apparently one of the most important of these properties is that v_{xc} should be such that the total effective potential is self-interaction free, meaning that an electron should not interact with itself via the Coulomb potential [61].

By this the following is meant:

From our Eq. (4.35) we see that the expression used for the Coulomb energy is

$$\frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.1)$$

where

$$n(\mathbf{r}) = \sum_i^{\text{occ.}} |\varphi_i(\mathbf{r})|^2; \quad (5.2)$$

$\sum_i^{\text{occ.}}$ denotes summation over all occupied Kohn-Sham orbitals $\varphi_i(\mathbf{r})$.

Now, when there is only one electron and hence only one Kohn-Sham orbital $\varphi_1(\mathbf{r})$, the expression for the Coulomb energy reads

$$\frac{1}{2} \int \int \frac{|\varphi_1(\mathbf{r})|^2 |\varphi_1(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.3)$$

which does not vanish as it actually should since a single electron does not lead to any Coulomb energy.

But just as a single electron must not interact with itself via Coulomb's law, so the individual electrons of a many-electron system also must not interact with themselves via Coulomb's law; however, such a self-interaction is contained in the usual ansatz Eq. (5.1) as we have seen in the special case of a single electron.

One approach to this problem is to subtract the self-interaction of the electrons which occurs in the Coulomb potential by means of some correction to the potential.

This usually leads to orbital-dependent potentials, i.e., instead of a universal exchange-correlation potential $v_{xc}(\mathbf{r})$, in Eq. (4.38) an orbital-dependent $v_{xci}(\mathbf{r})$ has to be used which is different for different orbital index i .

Surely, this approach is consequently outside the DFT formalism. Nevertheless, the results obtained using these orbital-dependent self-interaction corrections (SIC) are encouraging [61, 105], in particular as far as band gap values are concerned.

This made scientist think about possible SIC approaches leading to universal, orbital-independent functionals $v_{xc}(\mathbf{r})$.

Of course, this aim will always be achieved when we go the formally correct way, i.e., we first choose some exchange-correlation energy functional $E_{xc}[n]$ and then determine $v_{xc}(\mathbf{r})$ by forming its functional derivative with respect to the electron density,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (5.4)$$

To be able to make a good choice for the functional $E_{xc}[n]$ we recall that it should cancel the electron self-interactions contained in the Coulomb energy functional.

In order to find these we use Eq. (5.2) to rewrite the expression for the Coulomb energy Eq. (5.1):

$$\begin{aligned} \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' &= \frac{1}{2} \int \int \frac{\sum_i^{\text{occ.}} |\varphi_i(\mathbf{r})|^2 \sum_j^{\text{occ.}} |\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{2} \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \int \int \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{2} \sum_i^{\text{occ.}} \sum_{j \neq i}^{\text{occ.}} \int \int \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &\quad + \frac{1}{2} \sum_i^{\text{occ.}} \int \int \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (5.5)$$

and from this we see that the self-interaction contributions are given by

$$\begin{aligned}
& \frac{1}{2} \sum_i^{\text{occ.}} \int \int \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
&= \frac{1}{2} \sum_i^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{5.6}
\end{aligned}$$

We see from the Hartree-Fock equations (4.25) that in the Hartree-Fock method self-Coulomb and self-exchange cancel exactly. There is no self-energy in Hartree-Fock theory.

Therefore it seems worth while to try with the corresponding Fock exchange energy expression

$$-\frac{1}{2} \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{5.7}$$

It is quite obvious that this expression will achieve the required cancellation of the self-interaction (5.6) since it can be decomposed as

$$\begin{aligned}
& -\frac{1}{2} \sum_i^{\text{occ.}} \sum_{j \neq i}^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \\
& -\frac{1}{2} \sum_i^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_i^*(\mathbf{r}') \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{5.8}
\end{aligned}$$

Note, however, that even though this way we use the same expression for the energy as in Hartree-Fock theory we will not arrive at the Hartree-Fock method since the Hartree-Fock method contains the minimization of the total energy with respect to the individual electron wave functions as a central idea, whereas in DFT the minimization is with respect to the total electron density.

The expression Eq. (5.7) is generally known as the exact exchange (EXX) energy and is often used as exchange energy functional $E_x[n]$, i.e., as part of the exchange-correlation energy functional $E_{xc}[n] = E_x[n] + E_c[n]$.

In particular, schemes using this exact exchange E_x , Eq. (5.7), without an additional correlation energy part E_c , so-called exact exchange only (EXX-only) schemes, have proven to produce good results for band gap values [59, 109, 112, 113].

We, too, will therefore focus on such schemes in the remainder of this work.

However, although we now have a suitable expression for the exchange-correlation energy functional, namely the exact exchange energy, Eq. (5.7),

$$E_{xc}[n] := E_x[n] := -\frac{1}{2} \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \tag{5.9}$$

we still have to find the corresponding expression for the potential

$$v_{\text{xc}}(\mathbf{r}) := v_{\text{x}}(\mathbf{r}) = \frac{\delta E_{\text{x}}[n]}{\delta n(\mathbf{r})} \quad (5.10)$$

which is needed in Eq. (4.38) when we want to carry out a Kohn-Sham calculation scheme.

We will see in section 5.3 that this determination of the exact exchange potential v_{x} is not at all a trivial problem and in the following sections we make the acquaintance of some approaches to solve it approximately.

5.3 The problem to determine the exact exchange potential

In this section we want to have a look at the problem of determining the exchange-correlation potential $v_{xc}(\mathbf{r})$ defined by

$$v_{xc}(\mathbf{r}) := \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (5.11)$$

In section 5.2 we agreed to use for the exchange-correlation energy functional $E_{xc}[n]$ the so-called exact exchange energy functional

$$E_x[n] = -\frac{1}{2} \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \int \int \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.12)$$

and hence we have to face the problem of determining the exact exchange potential

$$v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} \quad (5.13)$$

with $E_x[n]$ given by Eq. (5.12).

We recall from section 4.1 how such a functional derivative is defined:

From Eq. (4.8) we see that to determine $\frac{\delta E_x[n]}{\delta n(\mathbf{r})}$ directly, we have to know to first order the $\Delta E_x[n]$ by which $E_x[n]$ changes when a small change $\Delta n(\mathbf{r})$ in the electron density $n(\mathbf{r})$ occurs.

However, in our formula Eq. (5.12) for the exact exchange energy the electron density $n(\mathbf{r})$ does not occur as explicit variable, but only the one-particle Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ do.

Consequently, to find the $\Delta E_x[n]$ corresponding to some $\Delta n(\mathbf{r})$ we first have to know the $\Delta \varphi_i(\mathbf{r})$ corresponding to $\Delta n(\mathbf{r})$.

The relationship between $n(\mathbf{r})$ and the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ is

$$n(\mathbf{r}) = \sum_i^{\text{occ.}} |\varphi_i(\mathbf{r})|^2; \quad (5.14)$$

this, however, does not allow the calculation of the $\varphi_i(\mathbf{r})$ from $n(\mathbf{r})$ and there is no easy relationship known which allows this. The whole complexity of the many-particle problem seems to be hidden behind this question.

Nevertheless, we will try in section 7.1 to determine $v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})}$ in the just described way approximately by using the chain rule for functional derivatives and a self-made approximation for $\frac{\delta \varphi_i(\mathbf{r}')}{\delta n(\mathbf{r})}$.

But first, in section 5.4 we have a look at how scientists proceeded in the past years to determine $v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})}$ in spite of the mentioned difficulties.

5.4 Methods to evaluate the exact exchange potential

For now and all remaining sections we want to generalize our formalism to the spin-unrestricted case.

This essentially means that we get an additional spin-index σ for some of our functions where σ is either \uparrow (spin-up) or \downarrow (spin-down).

In particular, we are now dealing with spin-dependent Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$ with corresponding one-particle eigenvalues $\varepsilon_{1\sigma} \leq \varepsilon_{2\sigma} \leq \dots$; we denote the number of occupied Kohn-Sham orbitals with spin σ as N_σ .

The spin-densities $n_\sigma(\mathbf{r})$ are then given as

$$n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \quad (5.15)$$

and the total electron density is

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} n_\sigma(\mathbf{r}). \quad (5.16)$$

The exact exchange energy functional now reads

$$E_x[n] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \int \int \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.17)$$

and in the Kohn-Sham scheme, instead of Eq. (4.38) we use

$$\left(-\frac{1}{2} \nabla^2 + v_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc\sigma}([n]; \mathbf{r}) \right) \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}), \quad \varepsilon_{1\sigma} \leq \varepsilon_{2\sigma} \leq \dots \quad (5.18)$$

where

$$v_{xc\sigma}([n]; \mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n_\sigma(\mathbf{r})}. \quad (5.19)$$

Consequently, the problem we are facing is the determination of the exact exchange potential functions

$$v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})}, \sigma \in \{\uparrow, \downarrow\} \quad (5.20)$$

with the exact exchange energy functional $E_x[n]$ given by Eq. (5.17) and the spin-densities $n_\sigma(\mathbf{r})$ given by Eq. (5.15).

The method which Kotani [109, 112] uses to determine $v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})}$ is based on the chain rule for functional derivatives applied in the form

$$\frac{\delta E_x[n]}{\delta v_{s\sigma}(\mathbf{r})} = \int \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r}')} \frac{\delta n_\sigma(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})} d\mathbf{r}'. \quad (5.21)$$

Hereby $v_{s\sigma}(\mathbf{r})$ denotes the effective spin-dependent potential which already occurred in its spin-independent form $v_s(\mathbf{r})$ in Eqs. (4.32), (4.34), and (4.36). $\frac{\delta n_\sigma(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})}$ can be determined from the results of perturbation theory from which we know how the wave functions and hence how the spin-densities react to small variations in the potential functions. In particular, to first order only $n_\uparrow(\mathbf{r}')$ reacts to small changes in $v_{s\uparrow}(\mathbf{r})$ and the same is true for $\sigma = \downarrow$; this is why in Eq. (5.21) no spin-summation occurs.

Now, Kotani uses Eq. (5.21) in a special program context, namely in a linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) program. There the crystal volume is split up into overlapping spheres. He indexes these spheres by some index R and furthermore assumes the density and potential functions to be spherically symmetric inside the spheres.

Then, by (r, R) denoting a point inside the sphere R which has a distance r from the center of the sphere, he can rewrite Eq. (5.21) as

$$\frac{\delta E_x[n]}{\delta v_{s\sigma}(r, R)} = \sum_{R'} \int_0^{\bar{R}'} \frac{\delta E_x[n]}{\delta n_\sigma(r', R')} \frac{\delta n_\sigma(r', R')}{\delta v_{s\sigma}(r, R)} dr' \quad (5.22)$$

(cf. Eq. (13) in Ref. [112]) where by \bar{R}' he denotes the radius of the sphere R' . Kotani in addition applies some partially program specific tricks to determine $\frac{\delta E_x[n]}{\delta v_{s\sigma}(r, R)}$ and then uses the trapezoidal integration method to transform Eq. (5.22) into a linear equation. From the so obtained linear equations he then calculates $\frac{\delta E_x[n]}{\delta n_\sigma(r', R')}$ for a number of r' -values.

The other ways which are taken to determine $v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})}$ usually rely on the chain rule for functional derivatives in the form

$$\begin{aligned} v_{x\sigma}(\mathbf{r}) &= \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' \\ &\quad + \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}^*(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}^*(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' \\ &= \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' + c.c. \end{aligned} \quad (5.23)$$

where *c.c.* denotes the complex conjugate of the expression preceding it.

The chain rule for functional derivatives is then applied once more to $\frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}$, namely as

$$\frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} = \sum_{\beta=\uparrow,\downarrow} \int \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}''. \quad (5.24)$$

Since both the potential functions and the spin-densities are real valued this all in all leads to

$$v_{x\sigma}(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow} \sum_{\beta=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \int \left(\frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} + c.c. \right) \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' d\mathbf{r}''. \quad (5.25)$$

Actually, the sums over α and β finally vanish and instead of the α 's and β 's only the index σ occurs.

Görling and co-workers [113, 114, 115] in the framework of a pseudopotential program now proceed as follows to determine $v_{x\sigma}(\mathbf{r})$:

First they choose plane-wave basis sets for the expansion of the wave functions, the density functions and the potential functions. Then they determine vector and matrix representations of the functional derivatives occurring in Eq. (5.25); the matrix representation of $\frac{\delta v_{s\sigma}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}$ is hereby obtained by inverting the matrix representation of $\frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}'')}$; the representations of $\frac{\delta \varphi_{i\sigma}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r}'')}$ and $\frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}'')}$ are determined with the help of perturbation theory.

From the so obtained vector and matrix representations they finally obtain a vector representation of $v_{x\sigma}(\mathbf{r})$ in the chosen basis.

Now there are two more approaches to the determination of the exact exchange potential $v_{x\sigma}(\mathbf{r})$ left which we want to describe, namely the optimized effective potential (OEP) method [103, 107, 110] and the Krieger-Li-Iafrate (KLI) method [51, 54, 90].

The equations for both these methods can be obtained starting with the above Eq. (5.25) and in fact the KLI method is "simply" a very good working approximation to the OEP method but is much less demanding from a numerical point of view.

The complete next chapter, chapter 6, is dedicated to the KLI method. There we describe the OEP and the KLI methods in detail, we see that the KLI method is in fact a very promising approach and we focus on the possibility to adapt it to certain programs of ours.

One reason why we drop both Kotani's and Görling's approaches is the fact that their approaches are from the very beginning quite closely tailored to the particular programs they use whereas the OEP and KLI approaches are much more general and therefore better suited for our purposes.

6. The Krieger-Li-Iafrate (KLI) approach

6.1 The Krieger-Li-Iafrate (KLI) method in detail

In this section we explain the Krieger-Li-Iafrate (KLI) method and describe how it can be derived.

The KLI method provides a numerically feasible way for obtaining good approximations to the exact exchange potential $v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})}$ with the exact exchange energy $E_x[n]$ given by Eq. (5.17). The KLI method is in fact an approximation to the so-called optimized effective potential (OEP) method and therefore we start with the description and derivation of the OEP method.

The "OEP method" consists mainly of the OEP integral equation which has to be solved numerically to obtain the exact exchange potential. This integral equation is actually not a very recent discovery but was already given by Sharp and Horton in 1953 (see Eq. (2) in Ref. [110]).

Sharp and Horton [110] and also Talman and Shadwick [107] derive this integral equation by looking for so-called optimized effective potentials

$$v_{s\sigma}^{\text{OEP}}(\mathbf{r}) = v_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{x\sigma}(\mathbf{r}) \quad (6.1)$$

which minimize the total energy functional $E_{\text{tot}}[n]$ given by

$$\begin{aligned} E_{\text{tot}}[n] = & \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \int \varphi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_{i\sigma}(\mathbf{r}) d\mathbf{r} \\ & + \int v_0(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & + E_x[n] \end{aligned} \quad (6.2)$$

where $E_x[n]$ is the exact exchange energy functional given by Eq. (5.17); i.e., they start from the problem

$$\left. \frac{\delta E_{\text{tot}}}{\delta v_{s\sigma}(\mathbf{r})} \right|_{v=v^{\text{OEP}}} = 0. \quad (6.3)$$

(However, the OEP method can equally well be applied to some $E_{\text{tot}}[n]$ with an arbitrary density functional $E_{\text{xc}}[n]$ instead of the exact exchange energy functional $E_x[n]$ in Eq. (6.2).)

The resulting OEP integral equations for the exact exchange potential can be written as [116]

$$\sum_{i=1}^{N_\sigma} \int (v_{x\sigma}^{\text{OEP}}(\mathbf{r}') - u_{xi\sigma}(\mathbf{r}')) G_{Si\sigma}(\mathbf{r}'; \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') d\mathbf{r}' + c.c. = 0 \quad (6.4)$$

where

$$u_{xi\sigma}(\mathbf{r}) = -\frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.5)$$

and

$$G_{Si\sigma}(\mathbf{r}'; \mathbf{r}) = \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}}. \quad (6.6)$$

In order to be able to solve the OEP integral equation approximately, Sharp and Horton [110] approximate the eigenvalues $\varepsilon_{k\sigma}$ in Eq. (6.6) by a suitable average value $\varepsilon_{0i\sigma}$. Their approximate solution for $v_{x\sigma}(\mathbf{r})$ then is

$$v_{x\sigma}(\mathbf{r}) = -\frac{1}{2} \frac{\sum_{i=1}^{N_\sigma} \sum_{k=1}^{N_\sigma} \frac{\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{0i\sigma}} \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'}{\sum_{i=1}^{N_\sigma} \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{0i\sigma}}} + c.c. \quad (6.7)$$

(cf. Eq. (4) in Ref. [110]).

Sharp and Horton [110] also note that when one makes in Eq. (6.7) the further approximation that all $\varepsilon_i - \varepsilon_{0i\sigma}$ are equal, Eq. (6.7) further simplifies to

$$v_{x\sigma}(\mathbf{r}) = -\frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \sum_{k=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + c.c. \quad (6.8)$$

which is the "Slater exchange potential" obtained by Slater in 1951 [26]. Slater obtained it by forming a weighted average of the Hartree-Fock potential functions; the weight that has to be used hereby to weight the Hartree-Fock potential function for the orbital $\varphi_{i\sigma}(\mathbf{r})$ is

$$\frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})}. \quad (6.9)$$

We now present a derivation of the OEP integral equations. However, we do not start from the ansatz Eq. (6.3) used by Sharp and Horton [110] and Talman and Shadwick [107] but from the equivalent ansatz

$$v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})}. \quad (6.10)$$

The derivation which we now describe was first given by Görling and Levy [114]. Our presentation follows that of Ref. [116].

First of all, since the exact exchange energy functional

$$E_x[n] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \int \int \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (6.11)$$

Eq. (5.17), does not depend explicitly on the spin-densities $n_\sigma(\mathbf{r})$ but only on the Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$, the chain rule for functional derivatives is applied to Eq. (6.10) to give

$$\begin{aligned} v_{x\sigma}(\mathbf{r}) &= \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' \\ &\quad + \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}^*(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}^*(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' \\ &= \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' + c.c. \end{aligned} \quad (6.12)$$

From Eq. (6.11) we see that a small change $\Delta \varphi_{i\alpha}(\mathbf{r}')$ in $\varphi_{i\alpha}(\mathbf{r}')$ results in the following first-order change ΔE_x in E_x :

$$\begin{aligned} \Delta E_x &= -\frac{1}{2} \sum_{j=1}^{N_\alpha} \int \int \frac{\varphi_{i\alpha}^*(\mathbf{r}) \varphi_{j\alpha}^*(\mathbf{r}') \varphi_{j\alpha}(\mathbf{r}) \Delta \varphi_{i\alpha}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &\quad - \frac{1}{2} \sum_{j=1}^{N_\alpha} \int \int \frac{\varphi_{j\alpha}^*(\mathbf{r}') \varphi_{i\alpha}^*(\mathbf{r}) \Delta \varphi_{i\alpha}(\mathbf{r}') \varphi_{j\alpha}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (6.13)$$

Recalling Eq. (4.8) defining the concept of functional derivation we see that $\frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')}$ is given by

$$\begin{aligned} \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} &= -\sum_{j=1}^{N_\alpha} \int \frac{\varphi_{i\alpha}^*(\mathbf{r}) \varphi_{j\alpha}^*(\mathbf{r}') \varphi_{j\alpha}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \\ &= -\sum_{j=1}^{N_\alpha} \varphi_{j\alpha}^*(\mathbf{r}') \int \frac{\varphi_{i\alpha}^*(\mathbf{r}''') \varphi_{j\alpha}(\mathbf{r}''')}{|\mathbf{r}' - \mathbf{r}'''|} d\mathbf{r}'''. \end{aligned} \quad (6.14)$$

However, we do not know how to obtain the functional derivative $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}$ occurring in Eq. (6.12) directly.

To be able to calculate it after all, we apply the chain rule for functional derivatives to $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}$ using our knowledge that there is a one-to-one correspondence between ground state electron densities and ground state potential functions and between the ground state Kohn-Sham orbitals and the ground state potential functions [31]:

$$\begin{aligned}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} &= \sum_{\beta=\uparrow,\downarrow} \int \frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}'' \\ \frac{\delta\varphi_{i\alpha}^*(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} &= \sum_{\beta=\uparrow,\downarrow} \int \frac{\delta\varphi_{i\alpha}^*(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}''.\end{aligned}\quad (6.15)$$

Eq. (6.12) can then be rewritten as

$$v_{x\sigma}(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow} \sum_{\beta=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \int \left(\frac{\delta E_x[n]}{\delta\varphi_{i\alpha}(\mathbf{r}')} \frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} + c.c. \right) \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' d\mathbf{r}''. \quad (6.16)$$

From perturbation theory we know that a small change $\Delta v_{s\beta}(\mathbf{r}'')$ in the effective potential $v_{s\beta}(\mathbf{r}'')$ results in the following first-order change $\Delta\varphi_{i\alpha}(\mathbf{r}')$ in $\varphi_{i\alpha}(\mathbf{r}')$:

$$\Delta\varphi_{i\alpha}(\mathbf{r}') = \delta_{\alpha\beta} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\int \varphi_{k\beta}^*(\mathbf{r}'') \Delta v_{s\beta}(\mathbf{r}'') \varphi_{i\beta}(\mathbf{r}'') d\mathbf{r}''}{\varepsilon_{i\beta} - \varepsilon_{k\beta}} \varphi_{k\beta}(\mathbf{r}') \quad (6.17)$$

where $\delta_{\alpha\beta}$ is the Kronecker-delta:

$$\delta_{\alpha\beta} = \begin{cases} 0 & \text{if } \alpha \neq \beta \\ 1 & \text{if } \alpha = \beta \end{cases}. \quad (6.18)$$

Considering Eq. (4.9) defining functional derivation in cases like the present one, we see that $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')}$ is given by

$$\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} = \delta_{\alpha\beta} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\beta}^*(\mathbf{r}'') \varphi_{k\beta}(\mathbf{r}')}{\varepsilon_{i\beta} - \varepsilon_{k\beta}} \varphi_{i\beta}(\mathbf{r}''). \quad (6.19)$$

Now, in Eq. (6.16) only the functional derivative $\frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})}$ is unknown.

But at least we know the inverse of this functional derivative,

$$\frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\beta}(\mathbf{r}'')} = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta n_\sigma(\mathbf{r})}{\delta\varphi_{i\alpha}(\mathbf{r}''')} \frac{\delta\varphi_{i\alpha}(\mathbf{r}''')}{\delta v_{s\beta}(\mathbf{r}'')} d\mathbf{r}''' + c.c. : \quad (6.20)$$

$\frac{\delta \varphi_{i\alpha}(\mathbf{r}''')}{\delta v_{s\beta}(\mathbf{r}'')}$ is known from Eq. (6.19) and from $n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})$ we see that to a small change $\Delta \varphi_{i\alpha}(\mathbf{r}''')$ in $\varphi_{i\alpha}(\mathbf{r}''')$ corresponds the following first-order change $\Delta n_\sigma(\mathbf{r})$ in $n_\sigma(\mathbf{r})$:

$$\begin{aligned} \Delta n_\sigma(\mathbf{r}) &= \delta_{\alpha\sigma} \varphi_{i\alpha}^*(\mathbf{r}) \Delta \varphi_{i\alpha}(\mathbf{r}) \\ &= \delta_{\alpha\sigma} \int \varphi_{i\alpha}^*(\mathbf{r}) \Delta \varphi_{i\alpha}(\mathbf{r}''') \delta(\mathbf{r} - \mathbf{r}''') d\mathbf{r}''' \end{aligned} \quad (6.21)$$

where $\delta(\mathbf{r} - \mathbf{r}''')$ denotes the Dirac delta function.

Hence, $\frac{\delta n_\sigma(\mathbf{r})}{\delta \varphi_{i\alpha}(\mathbf{r}''')}$ is given by

$$\frac{\delta n_\sigma(\mathbf{r})}{\delta \varphi_{i\alpha}(\mathbf{r}''')} = \delta_{\alpha\sigma} \varphi_{i\alpha}^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'''). \quad (6.22)$$

From (6.20), (6.22), and (6.19) we see

$$\begin{aligned} \frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\beta}(\mathbf{r}'')} &= \delta_{\beta\sigma} \sum_{i=1}^{N_\sigma} \varphi_{i\sigma}^*(\mathbf{r}) \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(\mathbf{r}'') \varphi_{k\sigma}(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}'') + c.c. \\ &= \delta_{\beta\sigma} \sum_{i=1}^{N_\sigma} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}'') \varphi_{k\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}'')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} + c.c. \end{aligned} \quad (6.23)$$

Of course, this implies that in Eq. (6.16) there is only a non-vanishing contribution for $\beta = \sigma$.

Performing on both sides of Eq. (6.16) the operation

$$\int \frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}''')} d\mathbf{r}, \quad (6.24)$$

the left hand side becomes

$$\int v_{x\sigma}(\mathbf{r}) \frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}''')} d\mathbf{r} \quad (6.25)$$

and in the right hand side using the chain rule for functional derivatives the following simplification is possible:

$$\int \frac{\delta v_{s\sigma}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} \frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}''')} d\mathbf{r} = \frac{\delta v_{s\sigma}(\mathbf{r}'')}{\delta v_{s\sigma}(\mathbf{r}''')} \quad (6.26)$$

and since a change $\Delta v_{s\sigma}(\mathbf{r}''')$ in $v_{s\sigma}(\mathbf{r}''')$ leads to the change

$$\Delta v_{s\sigma}(\mathbf{r}'') = \int \Delta v_{s\sigma}(\mathbf{r}''') \delta(\mathbf{r}'' - \mathbf{r}''') d\mathbf{r}''' \quad (6.27)$$

in $v_{s\sigma}(\mathbf{r}'')$, we have

$$\frac{\delta v_{s\sigma}(\mathbf{r}'')}{\delta v_{s\sigma}(\mathbf{r}''')} = \delta(\mathbf{r}'' - \mathbf{r}'''). \quad (6.28)$$

All in all, Eq. (6.16) then becomes

$$\int v_{x\sigma}(\mathbf{r}) \frac{\delta n_{\sigma}(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}''')} d\mathbf{r} = \sum_{i=1}^{N_{\sigma}} \int \left(\frac{\delta E_x[n]}{\delta \varphi_{i\sigma}(\mathbf{r}')} \frac{\delta \varphi_{i\sigma}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r}''')} + c.c. \right) d\mathbf{r}' \quad (6.29)$$

where we have already used the $\delta_{\alpha\beta}$ occurring in Eq. (6.19).

Now we gather our results Eqs. (6.23), (6.14), and (6.19) and rewrite Eq. (6.29) as

$$\begin{aligned} & \int v_{x\sigma}(\mathbf{r}) \sum_{i=1}^{N_{\sigma}} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}''') \varphi_{k\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}''')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} d\mathbf{r} + c.c. \\ &= - \sum_{i=1}^{N_{\sigma}} \int \left(\sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}') \int \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(\mathbf{r}''') \varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}''') + c.c. \right) d\mathbf{r}'. \end{aligned} \quad (6.30)$$

This is equivalent to

$$\begin{aligned} & \sum_{i=1}^{N_{\sigma}} \int v_{x\sigma}(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') d\mathbf{r}' + c.c. \\ &= \sum_{i=1}^{N_{\sigma}} \int \left(-\frac{1}{\varphi_{i\sigma}^*(\mathbf{r}')} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}') \int \frac{\varphi_{i\sigma}^*(\mathbf{r}'') \varphi_{j\sigma}(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} d\mathbf{r}'' \right) \times \\ & \times \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') d\mathbf{r}' + c.c. \end{aligned} \quad (6.31)$$

Recalling the previously introduced abbreviations $u_{xi\sigma}(\mathbf{r})$, Eq. (6.5), and $G_{Si\sigma}(\mathbf{r}'; \mathbf{r})$, Eq. (6.6), this is just the OEP integral equation (6.4).

Let us now introduce the KLI approximation to the OEP integral equation (6.4).

Since the full OEP integral equation is numerically highly demanding, Krieger, Li, and Iafrate [54] made the suggestion to approximate the differences $\varepsilon_{i\sigma} - \varepsilon_{k\sigma}$ occurring in the formula for $G_{Si\sigma}(\mathbf{r}'; \mathbf{r})$, Eq. (6.6), by some average value $\Delta\varepsilon$.

Furthermore using the completeness relation

$$\sum_{k=1}^{\infty} \varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'), \quad (6.32)$$

$G_{Si\sigma}(\mathbf{r}'; \mathbf{r})$ is then approximated by

$$G_{Si\sigma}(\mathbf{r}'; \mathbf{r}) \approx \frac{1}{\Delta\varepsilon} (\delta(\mathbf{r} - \mathbf{r}') - \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r})). \quad (6.33)$$

Introducing the abbreviations

$$\bar{u}_{xj\sigma} = \int u_{xj\sigma}(\mathbf{r}) |\varphi_{j\sigma}(\mathbf{r})|^2 d\mathbf{r}, \quad (6.34)$$

$$\bar{v}_{xj\sigma}^{\text{KLI}} = \int v_{x\sigma}^{\text{KLI}}(\mathbf{r}) |\varphi_{j\sigma}(\mathbf{r})|^2 d\mathbf{r}, \quad (6.35)$$

we apply the approximation Eq. (6.33) to the OEP integral equation (6.4) and perform the following equivalence transformations:

$$\begin{aligned} & \sum_{i=1}^{N_\sigma} \int (v_{x\sigma}^{\text{KLI}}(\mathbf{r}') - u_{xi\sigma}(\mathbf{r}')) \frac{1}{\Delta\varepsilon} (\delta(\mathbf{r} - \mathbf{r}') - \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r})) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') d\mathbf{r}' + c.c. = 0, \\ & \sum_{i=1}^{N_\sigma} \left[- \int (v_{x\sigma}^{\text{KLI}}(\mathbf{r}') - u_{xi\sigma}(\mathbf{r}')) \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') d\mathbf{r}' \right] + c.c. = 0, \\ & \left[v_{x\sigma}^{\text{KLI}}(\mathbf{r}) n_\sigma(\mathbf{r}) - \sum_{i=1}^{N_\sigma} (u_{xi\sigma}(\mathbf{r}) |\varphi_{i\sigma}(\mathbf{r})|^2 + \bar{v}_{xi\sigma}^{\text{KLI}} |\varphi_{i\sigma}(\mathbf{r})|^2 - \bar{u}_{xi\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2) \right] + c.c. = 0, \\ & v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 [(u_{xi\sigma}(\mathbf{r}) + (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})) + c.c.]. \end{aligned} \quad (6.36)$$

Eq. (6.36) is the KLI equation; it allows the calculation of the KLI exchange potential functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ as soon as the functions $u_{xi\sigma}(\mathbf{r})$ and the numbers $\bar{v}_{xi\sigma}^{\text{KLI}}$, $\bar{u}_{xi\sigma}$ have been obtained.

Since we have an explicit formula for the $u_{xi\sigma}(\mathbf{r})$, Eq. (6.5), and the $\bar{u}_{xi\sigma}$ are given by Eq. (6.34), the only unknowns are the $\bar{v}_{xi\sigma}^{\text{KLI}}$ or, alternatively, the values $\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma}$ or $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$.

To get closer to our aim we introduce some more abbreviations

$$M_{ji\sigma} = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} d\mathbf{r} \quad (6.37)$$

and

$$\bar{V}_{xj\sigma}^S = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} (u_{xi\sigma}(\mathbf{r}) + u_{xi\sigma}^*(\mathbf{r})) d\mathbf{r}. \quad (6.38)$$

Now we perform on both sides of the KLI equation (6.36) the operation $\int |\varphi_{j\sigma}(\mathbf{r})|^2 d\mathbf{r}$ to obtain

$$\bar{v}_{xj\sigma}^{\text{KLI}} = \sum_{i=1}^{N_\sigma} \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \left[\frac{1}{2} (u_{xi\sigma}(\mathbf{r}) + u_{xi\sigma}^*(\mathbf{r})) + \bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right] d\mathbf{r},$$

$$\begin{aligned}
\bar{v}_{xj\sigma}^{\text{KLI}} &= \bar{V}_{xj\sigma}^S + \sum_{i=1}^{N_\sigma} M_{ji\sigma} \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right), \\
\bar{v}_{xj\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*) &= \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*) + \sum_{i=1}^{N_\sigma} M_{ji\sigma} \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right), \\
\sum_{i=1}^{N_\sigma} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) &= \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*). \quad (6.39)
\end{aligned}$$

In the remainder of this section we give a justification why one should set

$$\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma} = 0. \quad (6.40)$$

Once this has been done, the KLI potential functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ can be calculated as follows:

First the functions $u_{xi\sigma}(\mathbf{r})$, Eq. (6.5), the numbers $\bar{u}_{xi\sigma}$, Eq. (6.34), the numbers $M_{ji\sigma}$, Eq. (6.37), and the numbers $\bar{V}_{xj\sigma}^S$, Eq. (6.38), are calculated. Then a system of $N_\sigma - 1$ linear equations originating from Eq. (6.39) is solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$:

$$\begin{aligned}
\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) &= \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*), \\
j &= 1, \dots, N_\sigma - 1. \quad (6.41)
\end{aligned}$$

Finally, the functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ can be calculated from the KLI equation (6.36), recalling $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma} = 0$, Eq. (6.40).

Now let us see why we should make the choice $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma} = 0$:

For this, we examine the KLI equation (6.36) more closely, especially for $|\mathbf{r}| \rightarrow \infty$. For large $|\mathbf{r}|$ we have

$$\frac{|\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \rightarrow 0 \quad (6.42)$$

for all $i \neq N_\sigma$ since then $n_\sigma(\mathbf{r})$ is dominated by the highest occupied Kohn-Sham orbital, i.e., we have

$$|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 \approx n_\sigma(\mathbf{r}). \quad (6.43)$$

Consequently, for $|\mathbf{r}| \rightarrow \infty$ we have

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) \approx \frac{1}{2} [(u_{xN_\sigma\sigma}(\mathbf{r}) + (\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma})) + c.c.]. \quad (6.44)$$

From Eq. (6.5) we can see the behavior of $u_{xN_\sigma\sigma}(\mathbf{r})$ for $|\mathbf{r}| \rightarrow \infty$:

$$\begin{aligned}
u_{xN_\sigma\sigma}(\mathbf{r}) &\approx -\frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \frac{1}{|\mathbf{r}|} \delta_{ik} \\
&= -\frac{1}{r}. \quad (6.45)
\end{aligned}$$

But then, the limiting behavior of $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ is

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) \approx -\frac{1}{r} + \left(\frac{1}{2} (\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma}) + c.c. \right). \quad (6.46)$$

This consideration shows that the numbers $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma}$ are a degree of freedom determining an additive constant for the value of $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ in the range $|\mathbf{r}| \rightarrow \infty$.

The natural choice, of course, is to require $v_{x\sigma}^{\text{KLI}}(\mathbf{r}) \rightarrow 0$ for $|\mathbf{r}| \rightarrow \infty$ and this is why we demand $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma}$ to vanish.

But then, there is something else we can see from Eq. (6.46), namely that the KLI exchange potential functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ behave as $-\frac{1}{r}$ as $r \rightarrow \infty$.

This is an important property of the KLI exchange potential functions and we will come back to it in the following section, section 6.2.

Last but not least, we briefly compare the KLI exchange potential functions Eq. (6.36) with the approximate exchange potential functions Eq. (6.8) obtained by Sharp and Horton [110]. In fact, Eq. (6.8) can be obtained from Eq. (6.36) by simply setting all the $\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma}$ equal to zero, i.e., it is identical with

$$v_{x\sigma}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 [u_{xi\sigma}(\mathbf{r}) + c.c.]. \quad (6.47)$$

The reason for this discrepancy between the potential functions lies in the fact that Sharp and Horton actually approximate the function $G_{Si\sigma}(\mathbf{r}'; \mathbf{r})$, Eq. (6.6), by

$$G_{Si\sigma}(\mathbf{r}'; \mathbf{r}) \approx \frac{1}{\Delta_\varepsilon} \delta(\mathbf{r} - \mathbf{r}') \quad (6.48)$$

rather than by Eq. (6.33) (cf. footnote 4 in Ref. [110]).

6.2 Some properties of the KLI method

As we have seen in section 6.1, in going from the OEP to the KLI method a fairly crude approximation is made in setting all eigenvalue differences $\varepsilon_{i\sigma} - \varepsilon_{k\sigma}$ occurring in Eq. (6.6) equal to one and the same constant $\Delta\varepsilon$.

Therefore one need not expect the KLI approximation to be a particularly good one.

However, it has been shown that the KLI method has a number of properties which make it very promising. We say something about these in the present section. The next section, section 6.3, will then briefly tell about the quality of results obtained with the KLI method.

The first property of KLI we want to mention is that it is self-interaction free. This is already clear from the fact that KLI uses the exact exchange energy functional; we saw this connection in section 5.2. There we also explained why it is desirable to use a self-interaction free formalism.

A manifestation of the fact that KLI is self-interaction free is the $-\frac{1}{r}$ decay of the exchange potentials [116]; we noted this decay near the end of section 6.1.

Another advantage of KLI is that it produces a local and orbital-independent potential, i.e., potential functions fitting into the Kohn-Sham scheme, section 4.2. As we have seen in the sections 4.2–5.2, there are many formalisms in existence and in use which are not compatible with the Kohn-Sham scheme. Furthermore, orbital-independent potentials guarantee that the Kohn-Sham orbitals resulting from a Kohn-Sham calculation are orthogonal to each other. When using formalisms with orbital-dependent potentials one has to employ special computationally non-trivial tricks to ensure orthogonality of the resulting wave functions.

You might recall that in section 4.3 we introduced the concept of a discontinuity Δ_{xc} of the exchange-correlation potential and mentioned its probable importance for the calculation of good band gap values.

Now, whereas for example the exchange-correlation potentials obtained using LDA/LSD do not show such discontinuities [90], these discontinuities are correctly produced by the KLI exchange-correlation and in particular by the KLI exact exchange potentials [51, 54, 90].

Moreover, we just mention that the results of the KLI method satisfy Koopmans' theorem [117] and that the highest occupied single-particle state of each spin projection σ nearly exactly satisfies Janak's theorem [118] [52, 54].

KLI also shows the correct limiting behavior in the homogeneous-electron-gas limit, i.e., its results then reduce to the exact Kohn-Sham results [54].

6.3 The success of the KLI method

Since only a few solid state OEP or KLI calculations have been carried out which, however, in general produced improved band gap values [56, 59, 109, 112, 113, 119, 120, 121], in this section we concentrate on the success of KLI in atomic calculations.

As we have seen in section 4.2, the Hartree-Fock (HF) approach is constructed to give the best variational, i.e., the lowest, total energy: in this approach the wave functions are varied to minimize the total energy functional. Consequently, the total energies obtained by OEP or KLI have to be higher than those from HF. However, it turns out that both the OEP and the KLI results for the total energy and for the highest occupied spin orbital eigenvalues closely approximate the HF results for these values [51, 52, 54].

In particular, the KLI results are much better than those obtained by using other approximate exchange-only potentials like LDA/LSD exchange-only potentials or the exact Slater exchange potential which we mentioned in section 6.1.

In Ref. [54] some more "quality-tests" for the KLI results are described applying KLI to ten atoms with closed subshells. For example, the authors found out that the calculated electron density at the nucleus only differs by about 0.3% from the exact value; the expectation value $\langle r^2 \rangle$ of r^2 , which is proportional to the diamagnetic susceptibility, is closer to the exactly calculated value than the expectation values from similar calculations using different approximations for the exchange potential; the overlap integrals of the Kohn-Sham orbitals with the corresponding orbitals from OEP or HF yield values ≥ 0.999 .

Moreover, in section V of the same publication, good agreement of total energies, highest occupied single-particle eigenvalues, electron densities and spin-densities for alkali atoms is found between spin-unrestricted KLI, HF, and OEP.

6.4 KLI formulas for atomic calculations

In section 6.1 we have seen that the general proceeding in calculating the exact exchange potential functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ by the KLI method is the following:

First, the following functions and numbers are determined:

$$u_{xi\sigma}(\mathbf{r}) = -\frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.49)$$

$$\bar{u}_{xi\sigma} = \int u_{xi\sigma}(\mathbf{r}) |\varphi_{i\sigma}(\mathbf{r})|^2 d\mathbf{r} \quad (6.50)$$

$$M_{ji\sigma} = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} d\mathbf{r} \quad (6.51)$$

$$\bar{V}_{xj\sigma}^S = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} (u_{xi\sigma}(\mathbf{r}) + u_{xi\sigma}^*(\mathbf{r})) d\mathbf{r}. \quad (6.52)$$

Next, a system of $N_\sigma - 1$ linear equations is solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$:

$$\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) = \bar{V}_{xj\sigma}^S - \frac{1}{2}(\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*), \quad (6.53)$$

$j = 1, \dots, N_\sigma - 1.$

Finally, the function $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ can be calculated from

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 [(u_{xi\sigma}(\mathbf{r}) + (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})) + c.c.] \quad (6.54)$$

whereby $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \bar{u}_{xN_\sigma\sigma} = 0$.

Now, in the atomic context, the indices i of the Kohn-Sham orbitals contain the information about the principal quantum number n and the quantum numbers ℓ and m_ℓ from the angular solutions.

We therefore introduce the following notational conventions:

$$\begin{aligned} i &= (n, \ell, m_\ell) \\ k &= (n', \ell', m_{\ell'}) \\ j &= (n'', \ell'', m_{\ell''}) \end{aligned} \quad (6.55)$$

Moreover, the atomic Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$ can be written in terms of their radial parts $R_{n\ell\sigma}(r)$ and their angular parts $Y_L(\hat{\mathbf{r}})$, $L = (\ell, m_\ell)$, whereby by $Y_L(\hat{\mathbf{r}})$ we denote the real-valued spherical harmonics:

$$\varphi_{i\sigma}(\mathbf{r}) = R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}); \quad (6.56)$$

hereby $\hat{\mathbf{r}}$ denotes the polar angles of \mathbf{r} .

In the following we describe how the formulas (6.49)–(6.54) can be applied in the atomic context and in particular, all occurring integrals are reduced to radial integrals.

Before we start with this, note that it is in fact not necessary to calculate the functions $u_{x i \sigma}(\mathbf{r})$ explicitly, since in all other formulas only the products

$$\varphi_{i \sigma}^*(\mathbf{r}) u_{x i \sigma}(\mathbf{r}) = - \sum_{k=1}^{N_{\sigma}} \varphi_{k \sigma}^*(\mathbf{r}) \int \frac{\varphi_{i \sigma}^*(\mathbf{r}') \varphi_{k \sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.57)$$

are needed.

This saves us from the necessity to calculate a function containing a Kohn-Sham orbital in the denominator which might be zero at some points.

6.4.1 Calculation of the functions

$$\varphi_{i \sigma}^*(\mathbf{r}) u_{x i \sigma}(\mathbf{r}) =: (\varphi^* u_x)_{i \sigma}(\mathbf{r})$$

To calculate these functions, Eq. (6.57), we apply the relationship

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{r}}) \quad (6.58)$$

where $\tilde{r}_{<} (\tilde{r}_{>})$ denotes the smaller (greater) of r and r' ; this relationship is obtained from Eqs. (2.6.3) and (A.3.13) in Ref. [122].

Writing the Kohn-Sham orbitals in terms of their radial and angular parts, Eq. (6.57) can then be rewritten as follows:

$$\begin{aligned} (\varphi^* u_x)_{i \sigma}(\mathbf{r}) &= - \sum_{k=1}^{N_{\sigma}} R_{n' \ell' \sigma}^*(r) Y_{L'}(\hat{\mathbf{r}}) \int R_{n \ell \sigma}^*(r') R_{n' \ell' \sigma}(r') Y_L(\hat{\mathbf{r}}') Y_{L'}(\hat{\mathbf{r}}') \times \\ &\quad \times \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{r}}) d\mathbf{r}' \\ &= - \sum_{k=1}^{N_{\sigma}} R_{n' \ell' \sigma}^*(r) Y_{L'}(\hat{\mathbf{r}}) \int_0^{\infty} (r')^2 \int R_{n \ell \sigma}^*(r') R_{n' \ell' \sigma}(r') Y_L(\hat{\mathbf{r}}') Y_{L'}(\hat{\mathbf{r}}') \times \\ &\quad \times \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{r}}) d\hat{\mathbf{r}}' dr'. \end{aligned}$$

Now using real valued Gaunt integrals $C_{LL'L''}$ defined by

$$C_{LL'L''} = \int Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}) Y_{L''}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} \quad (6.59)$$

this can be further simplified:

$$\begin{aligned}
 (\varphi^* u_x)_{i\sigma}(\mathbf{r}) &= - \sum_{k=1}^{N_\sigma} R_{n'\ell'\sigma}^*(r) Y_{L'}(\hat{\mathbf{r}}) \int_0^\infty (r')^2 R_{n\ell\sigma}^*(r') R_{n'\ell'\sigma}(r') \times \\
 &\quad \times \sum_{L''} C_{LL'L''} \frac{4\pi}{2\ell''+1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}) dr'.
 \end{aligned}$$

Let S denote the unit sphere surface. The $Y_L(\hat{\mathbf{r}})$ form a complete orthonormal basis of $\mathcal{L}_2(S)$, i.e., of the set of all complex valued functions $f(\hat{\mathbf{r}})$ with

$$\int_0^{2\pi} \int_0^\pi |f(\hat{\mathbf{r}})|^2 \sin\theta d\theta d\varphi < \infty. \quad (6.60)$$

Since the $Y_L(\hat{\mathbf{r}})$ are bounded on the unit sphere surface, we can consequently write

$$Y_{L'}(\hat{\mathbf{r}}) Y_{L''}(\hat{\mathbf{r}}) = \sum_{L'''} a_{L'''} Y_{L'''}(\hat{\mathbf{r}}) \quad (6.61)$$

and multiplying both sides with $Y_L(\hat{\mathbf{r}})$, integrating over $\hat{\mathbf{r}}$, and using the orthonormality of the real valued spherical harmonics we find

$$a_{L'''} = \int Y_{L'}(\hat{\mathbf{r}}) Y_{L''}(\hat{\mathbf{r}}) Y_{L'''}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = C_{L'L''L'''}. \quad (6.62)$$

Now we can continue with our evaluation of $(\varphi^* u_x)_{i\sigma}(\mathbf{r})$:

$$\begin{aligned}
 (\varphi^* u_x)_{i\sigma}(\mathbf{r}) &= - \sum_{k=1}^{N_\sigma} R_{n'\ell'\sigma}^*(r) \int_0^\infty (r')^2 R_{n\ell\sigma}^*(r') R_{n'\ell'\sigma}(r') \times \\
 &\quad \times \sum_{L''} C_{LL'L''} \frac{4\pi}{2\ell''+1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} \sum_{L'''} C_{L'L''L'''} Y_{L'''}(\hat{\mathbf{r}}) dr' \\
 &= - \sum_{L'''} \sum_{k=1}^{N_\sigma} R_{n'\ell'\sigma}^*(r) \sum_{L''} \frac{4\pi}{2\ell''+1} C_{LL'L''} C_{L'L''L'''} \times \\
 &\quad \times \int_0^\infty (r')^2 \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} R_{n\ell\sigma}^*(r') R_{n'\ell'\sigma}(r') dr' Y_{L'''}(\hat{\mathbf{r}}).
 \end{aligned}$$

We consequently have

$$(\varphi^* u_x)_{i\sigma}(\mathbf{r}) = \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) \quad (6.63)$$

with

$$\begin{aligned}
 (\varphi^* u_x)_{i\sigma L'''}(r) &= - \sum_{k=1}^{N_\sigma} R_{n'\ell'\sigma}^*(r) \sum_{L''} \frac{4\pi}{2\ell''+1} C_{LL'L''} C_{L'L''L'''} \times \\
 &\quad \times \left(\frac{1}{r^{\ell''+1}} \int_0^r (r')^{\ell''+2} R_{n\ell\sigma}^*(r') R_{n'\ell'\sigma}(r') dr' + \right. \\
 &\quad \left. + r^{\ell''} \int_r^\infty (r')^{1-\ell''} R_{n\ell\sigma}^*(r') R_{n'\ell'\sigma}(r') dr' \right). \quad (6.64)
 \end{aligned}$$

6.4.2 Calculation of the numbers $\bar{u}_{xi\sigma}$

Using our result (6.63) and the orthonormality of the real valued spherical harmonics, Eq. (6.50) for $\bar{u}_{xi\sigma}$ can be written as

$$\begin{aligned}
 \bar{u}_{xi\sigma} &= \int \varphi_{i\sigma}^*(\mathbf{r}) u_{xi\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) d\mathbf{r} \\
 &= \int (\varphi^* u_x)_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) d\mathbf{r} \\
 &= \int \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}) d\mathbf{r} \\
 &= \int_0^\infty r^2 (\varphi^* u_x)_{i\sigma L}(r) R_{n\ell\sigma}(r) dr.
 \end{aligned} \tag{6.65}$$

6.4.3 Calculation of the numbers $M_{ji\sigma}$

For the calculation of the $M_{ji\sigma}$, Eq. (6.51), we assume that the spin-density $n_\sigma(\mathbf{r})$ has spherical symmetry, i.e., that it is given by $n_\sigma(r)$.

We then obtain

$$\begin{aligned}
 M_{ji\sigma} &= \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(r)} d\mathbf{r} \\
 &= \int \frac{|R_{n''\ell''\sigma}(r)|^2 (Y_{L''}(\hat{\mathbf{r}}))^2 |R_{n\ell\sigma}(r)|^2 (Y_L(\hat{\mathbf{r}}))^2}{n_\sigma(r)} d\mathbf{r} \\
 &= \int \frac{|R_{n''\ell''\sigma}(r)|^2 |R_{n\ell\sigma}(r)|^2}{n_\sigma(r)} \sum_{L'} C_{L'L''L''} Y_{L'}(\hat{\mathbf{r}}) (Y_L(\hat{\mathbf{r}}))^2 d\mathbf{r} \\
 &= \int_0^\infty \frac{r^2 |R_{n''\ell''\sigma}(r)|^2 |R_{n\ell\sigma}(r)|^2}{n_\sigma(r)} dr \sum_{L'} C_{L'L''L''} C_{LLL'}.
 \end{aligned} \tag{6.66}$$

6.4.4 Calculation of the numbers $\bar{V}_{xj\sigma}^S$

We again assume that the spin-density $n_\sigma(\mathbf{r})$ has spherical symmetry and is given by $n_\sigma(r)$. Furthermore using our result Eq. (6.63) we can rewrite Eq. (6.52) for $\bar{V}_{xj\sigma}^S$:

$$\begin{aligned}
 \bar{V}_{xj\sigma}^S &= \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(r)} \frac{1}{2} \left(\sum_{i=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) (\varphi^* u_x)_{i\sigma}(\mathbf{r}) + c.c. \right) d\mathbf{r} \\
 &= \Re \left\{ \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(r)} \sum_{i=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) (\varphi^* u_x)_{i\sigma}(\mathbf{r}) d\mathbf{r} \right\}
 \end{aligned} \tag{6.67}$$

$$\begin{aligned}
&= \Re \left\{ \int \frac{|R_{n''\ell''\sigma}(r)|^2 (Y_{L''}(\hat{\mathbf{r}}))^2}{n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} \left(R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}) \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) \right) d\mathbf{r} \right\} \\
&= \Re \left\{ \int \frac{|R_{n''\ell''\sigma}(r)|^2}{n_{\sigma}(r)} \sum_{L^{IV}} C_{L''L''L^{IV}} Y_{L^{IV}}(\hat{\mathbf{r}}) \times \right. \\
&\quad \left. \times \sum_{i=1}^{N_{\sigma}} R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}) \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) d\mathbf{r} \right\} \\
&= \Re \left\{ \int_0^{\infty} r^2 \frac{|R_{n''\ell''\sigma}(r)|^2}{n_{\sigma}(r)} \left(\sum_{i=1}^{N_{\sigma}} R_{n\ell\sigma}(r) \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) \right) \sum_{L^{IV}} C_{L''L''L^{IV}} C_{LL''L^{IV}} dr \right\}.
\end{aligned}$$

6.4.5 Calculation of the KLI exchange potential $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$

To be able to calculate the function $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ we first solve the system (6.53) of $N_{\sigma} - 1$ linear equations for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$, $i = 1, \dots, N_{\sigma} - 1$, and set $\bar{v}_{xN_{\sigma}\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xN_{\sigma}\sigma} + \bar{u}_{xN_{\sigma}\sigma}^*) = 0$.

Then we can calculate $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ from Eq. (6.54) which can be rewritten when we again assume $n_{\sigma}(\mathbf{r}) = n_{\sigma}(r)$ and use our result (6.63):

$$\begin{aligned}
v_{x\sigma}^{\text{KLI}}(\mathbf{r}) & \tag{6.68} \\
&= \frac{1}{2n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} [\varphi_{i\sigma}(\mathbf{r}) (\varphi^* u_x)_{i\sigma}(\mathbf{r}) + |\varphi_{i\sigma}(\mathbf{r})|^2 (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})] + c.c. \\
&= \frac{1}{2n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} \left[R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}) \sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) + \right. \\
&\quad \left. + |R_{n\ell\sigma}(r)|^2 (Y_L(\hat{\mathbf{r}}))^2 (\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)) \right] + c.c. \\
&= \frac{1}{2n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} R_{n\ell\sigma}(r) \sum_{L''} \left(\sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) C_{LL''L'''} + \right. \\
&\quad \left. + R_{n\ell\sigma}^*(r) (\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)) C_{LL''L''} \right) Y_{L''}(\hat{\mathbf{r}}) + c.c.
\end{aligned}$$

Here we are interested in the spherically symmetric part of the potential.

The spherically symmetric part of $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ is simply given by the contribution of $L'' = (\ell'', m_{\ell''}) = (0, 0)$.

We note

$$Y_{(0,0)}(\hat{\mathbf{r}}) = \frac{1}{\sqrt{4\pi}} \tag{6.69}$$

$$C_{L(0,0)L'''} = \int Y_L(\hat{\mathbf{r}}) \frac{1}{\sqrt{4\pi}} Y_{L'''}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \frac{1}{\sqrt{4\pi}} \delta_{LL'''}. \tag{6.70}$$

Consequently, the spherically symmetric part $v_{x\sigma}^{\text{KLI}}(r)$ of $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ is given by

$$\begin{aligned}
v_{x\sigma}^{\text{KLI}}(r) & \tag{6.71} \\
&= \frac{1}{2n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} R_{n\ell\sigma}(r) \left(\sum_{L'''} (\varphi^* u_x)_{i\sigma L'''}(r) \frac{1}{\sqrt{4\pi}} \delta_{LL'''} + \right. \\
&\quad \left. + R_{n\ell\sigma}^*(r) (\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)) \frac{1}{\sqrt{4\pi}} \right) \frac{1}{\sqrt{4\pi}} + c.c. \\
&= \frac{1}{8\pi n_{\sigma}(r)} \sum_{i=1}^{N_{\sigma}} R_{n\ell\sigma}(r) \left((\varphi^* u_x)_{i\sigma L}(r) + R_{n\ell\sigma}^*(r) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right) + c.c.
\end{aligned}$$

6.5 KLI formulas for the augmented spherical waves (ASW) method

In this section we want to see how the KLI formulas presented in section 6.1 can be implemented into the augmented spherical waves (ASW) program for band structure calculations [123].

The ASW program uses the so-called atomic sphere approximation (ASA) meaning that the whole crystal region is split into spheres around the atomic sites in such a way that the sum of the sphere volumes equals the crystal volume. The hereby necessarily occurring overlaps of spheres and the remaining interstitial regions are then treated in such a way that the crystal region can be considered as if it was the disjoint union of the constructed "atomic spheres". Of course, the attempt is made to keep the resulting mistakes as small as possible by making the overlaps and the remaining interstitial regions as small as possible.

A second important feature of the ASW program is that electron densities and potential functions are approximated by spherically symmetric functions inside each atomic sphere. Hence, for example all the information about the spin-density inside the atomic sphere around some site \mathbf{P} is given by a function

$$n_{\sigma}(r, \mathbf{P}), r \leq \bar{P} \quad (6.72)$$

where \bar{P} denotes the radius of the atomic sphere around \mathbf{P} .

The index i of the Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$ in the ASW program denotes the band index n together with some \mathbf{k} -vector from reciprocal space,

$$i = (n, \mathbf{k}), \quad (6.73)$$

and the Kohn-Sham orbitals can for \mathbf{r} inside an atomic sphere around site \mathbf{P} be written as

$$\varphi_{i\sigma}(\mathbf{r}) = \sum_L R_{i\sigma L}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \quad (6.74)$$

with radial functions $R_{i\sigma L}(r, \mathbf{P})$ and angular components $Y_L(\hat{\mathbf{r}}, \mathbf{P})$, the latter formed by real valued spherical harmonics. More details are given in the Appendix.

In the following we use for notational convenience notations (r, \mathbf{P}) and $(\hat{\mathbf{r}}, \mathbf{P})$ denoting coordinates relative to \mathbf{P} ; their meaning should be clear from Eqs. (6.72) and (6.74).

Before we apply the KLI formulas from section 6.1 to the ASW program we again collect them in their general form:

$$u_{xi\sigma}(\mathbf{r}) = -\frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \sum_{k=1}^{N_{\sigma}} \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.75)$$

$$\bar{u}_{xi\sigma} = \int u_{xi\sigma}(\mathbf{r}) |\varphi_{i\sigma}(\mathbf{r})|^2 d\mathbf{r} \quad (6.76)$$

$$M_{ji\sigma} = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_{\sigma}(\mathbf{r})} d\mathbf{r} \quad (6.77)$$

$$\bar{V}_{xj\sigma}^S = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} (u_{xi\sigma}(\mathbf{r}) + u_{xi\sigma}^*(\mathbf{r})) d\mathbf{r}. \quad (6.78)$$

The system of $N_{\sigma} - 1$ linear equations which has to be solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$ is

$$\sum_{i=1}^{N_{\sigma}-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) = \bar{V}_{xj\sigma}^S - \frac{1}{2}(\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*), \quad (6.79)$$

$$j = 1, \dots, N_{\sigma} - 1,$$

and the KLI exact exchange potentials are

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 [(u_{xi\sigma}(\mathbf{r}) + (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})) + c.c.] \quad (6.80)$$

with $\bar{v}_{xN_{\sigma}\sigma}^{\text{KLI}} - \bar{u}_{xN_{\sigma}\sigma} = 0$.

In the present context it turns out to be advantageous to calculate instead of the functions $u_{xi\sigma}(\mathbf{r})$ themselves, Eq. (6.75), the functions

$$\begin{aligned} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) &= -\varphi_{i\sigma}(\mathbf{r}) \sum_{k=1}^{N_{\sigma}} \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= -\sum_{k=1}^{N_{\sigma}} \varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \end{aligned} \quad (6.81)$$

We now describe how the necessary functions and numbers Eq. (6.81), Eqs. (6.76)–(6.78), and Eq. (6.80) can be calculated within the ASW program.

In the first approach we use fairly crude approximations to keep the computational effort low. In the second approach the formulas are simplified to a much smaller extent.

6.5.1 First approach

Calculation of the functions $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$

To make things easier we assume the products $\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r})$ to be spherically symmetric inside each atomic sphere.

For \mathbf{r} inside the atomic sphere around site \mathbf{P} $\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r})$ is due to Eq. (6.74) given by

$$\begin{aligned} \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}) &= \sum_L R_{i\sigma L}^*(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \sum_{L'} R_{k\sigma L'}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \\ &= \sum_{LL'} R_{i\sigma L}^*(r, \mathbf{P}) R_{k\sigma L'}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \\ &= \sum_{LL'L''} R_{i\sigma L}^*(r, \mathbf{P}) R_{k\sigma L'}(r, \mathbf{P}) C_{LL'L''} Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \end{aligned} \quad (6.82)$$

where in the last step we have applied the expansion of a product of spherical harmonics in terms of spherical harmonics, Eqs. (6.61) / (6.62).

Obviously the spherically symmetric part of $\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r})$ is now given by the $L'' = (0, 0)$ term of (6.82) for due to the orthonormality of the real valued spherical harmonics and

$$Y_{(0,0)}(\hat{\mathbf{r}}) = \frac{1}{\sqrt{4\pi}} \quad (6.83)$$

we have

$$\int Y_{L''}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = 0 \quad \text{for all } L'' \neq (0, 0). \quad (6.84)$$

Because of Eq. (6.83) and

$$C_{LL'(0,0)} = \frac{1}{\sqrt{4\pi}} \int Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \frac{1}{\sqrt{4\pi}} \delta_{LL'} \quad (6.85)$$

the spherically symmetric part of $\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r})$ inside the sphere around \mathbf{P} , we call it $(\varphi_{i\sigma}^* \varphi_{k\sigma})(r, \mathbf{P})$, is given by

$$\begin{aligned} (\varphi_{i\sigma}^* \varphi_{k\sigma})(r, \mathbf{P}) &= \sum_{LL'} R_{i\sigma L}^*(r, \mathbf{P}) R_{k\sigma L'}(r, \mathbf{P}) \frac{1}{\sqrt{4\pi}} \delta_{LL'} \frac{1}{\sqrt{4\pi}} \\ &= \frac{1}{4\pi} \sum_L R_{i\sigma L}^*(r, \mathbf{P}) R_{k\sigma L}(r, \mathbf{P}). \end{aligned} \quad (6.86)$$

Using the relationship

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{r}}), \quad (6.87)$$

Eq (6.58), where $\tilde{r}_{<} (\tilde{r}_{>})$ denotes the smaller (greater) of r and r' , and denoting the sphere around site \mathbf{P} by S_P we can for \mathbf{r} inside S_P approximately write $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$, Eq. (6.81), as

$$\begin{aligned}
& |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) \\
= & - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}'} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
= & - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \int_{S_P} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
& - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
= & - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \int_{S_P} (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) d\mathbf{r}' \\
& - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
\end{aligned}$$

— here $\tilde{r}_{<}(\tilde{r}_{>})$ denotes the smaller (greater) of (r, \mathbf{P}) and (r', \mathbf{P}) — and further

$$\begin{aligned}
& |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) \\
= & - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{L''} \sqrt{4\pi} \delta_{L''(0,0)} \times \\
& \times \int_0^{\bar{P}} (r', \mathbf{P})^2 (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} d(r', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \\
& - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
= & - 4\pi \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \times \\
& \times \left\{ \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 \frac{1}{(r, \mathbf{P})} (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\
& \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P})^2 \frac{1}{(r', \mathbf{P})} (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\
& - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
= & - 4\pi \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \left\{ \frac{1}{(r, \mathbf{P})} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\
& \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P}) (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\
& - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \int_{S_{P'}} \frac{(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \tag{6.88}
\end{aligned}$$

Due to the assumed spherical symmetry of $(\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}')$ inside the sphere around site \mathbf{P}' contributions from $\mathbf{P}' \neq \mathbf{P}$ can be regarded as being produced by

point charges

$$\begin{aligned} Q_{ik\sigma}^{\mathbf{P}'} &= \int_{S_{\mathbf{P}'}} (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}') d\mathbf{r}' \\ &= \int_0^{\bar{P}'} (r', \mathbf{P}')^2 \sum_L R_{i\sigma L}^* (r', \mathbf{P}') R_{k\sigma L} (r', \mathbf{P}') d(r', \mathbf{P}') \end{aligned} \quad (6.89)$$

located at the atomic sphere center \mathbf{P}' , i.e., for \mathbf{r} inside S_P we have

$$\begin{aligned} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) &= -4\pi \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*) (r, \mathbf{P}) \times \\ &\quad \times \left\{ \frac{1}{(r, \mathbf{P})} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ &\quad \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P}) (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\ &\quad - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*) (r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ik\sigma}^{\mathbf{P}'}}{|\mathbf{r} - \mathbf{P}'|}. \end{aligned} \quad (6.90)$$

In our general description of the ASW program at the beginning of this section we mentioned that both electron densities and potential functions are assumed to be spherically symmetric inside the atomic spheres. From Eq. (6.80) and the spherical symmetry inside the atomic spheres of the spin-densities $n_\sigma(\mathbf{r})$ we immediately notice that we only require the spherically symmetric part of the functions $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$ inside the atomic sphere around \mathbf{P} .

To obtain it, we have to set $|\mathbf{r} - \mathbf{P}'| \approx |\mathbf{P} - \mathbf{P}'|$ in the last term of Eq. (6.90) and then get

$$\begin{aligned} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) &= -4\pi \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*) (r, \mathbf{P}) \times \\ &\quad \times \left\{ \frac{1}{(r, \mathbf{P})} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ &\quad \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P}) (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\ &\quad - \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*) (r, \mathbf{P}) \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ik\sigma}^{\mathbf{P}'}}{|\mathbf{P} - \mathbf{P}'|} \end{aligned} \quad (6.91)$$

where

$$(\varphi_{i\sigma} \varphi_{k\sigma}^*) (r, \mathbf{P}) = \frac{1}{4\pi} \sum_L R_{i\sigma L} (r, \mathbf{P}) R_{k\sigma L}^* (r, \mathbf{P}) \quad (6.92)$$

$$(\varphi_{i\sigma}^* \varphi_{k\sigma}) (r, \mathbf{P}) = \frac{1}{4\pi} \sum_L R_{i\sigma L}^* (r, \mathbf{P}) R_{k\sigma L} (r, \mathbf{P}). \quad (6.93)$$

The only remaining difficulty in our formula Eq. (6.91) is the question how the sums

$$\sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ik\sigma}^{\mathbf{P}'}}{|\mathbf{P} - \mathbf{P}'|} \quad (6.94)$$

can be calculated.

From the definition of the $Q_{ik\sigma}^{\mathbf{P}'}$, Eq. (6.89), and from

$$\sum_{\mathbf{P}' \in UC} \int_{S_{\mathbf{P}'}} (\varphi_{i\sigma}^* \varphi_{k\sigma}) (r', \mathbf{P}') d\mathbf{r}' = \delta_{ik} \quad (6.95)$$

which is a consequence of the orthonormality of the Kohn-Sham orbitals we have

$$\sum_{\mathbf{P}'} Q_{ik\sigma}^{\mathbf{P}'} = 0 \quad \text{for } i \neq k \quad (6.96)$$

and

$$\sum_{\mathbf{P}'} \left(Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m} \right) = 0 \quad (6.97)$$

where m denotes the number of atomic spheres in a unit cell.

This implies that we can calculate the sums Eq. (6.94) for $i \neq k$ and the sums

$$\sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m}}{|\mathbf{P} - \mathbf{P}'|} \quad (6.98)$$

in complete analogy to the proceedings described in Eqs. (2.6.6)–(2.6.10) of Ref. [122], as is explained there.

From there we see that we have

$$\sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ik\sigma}^{\mathbf{P}'}}{|\mathbf{P} - \mathbf{P}'|} = \sum_{\mathbf{P}' \in UC(\mathbf{P})} \sqrt{4\pi} D_L(\mathbf{P} - \mathbf{P}', \mathbf{0}) Q_{ik\sigma}^{\mathbf{P}'} \Big|_{\ell=0, \kappa \rightarrow 0} \quad (6.99)$$

for $i \neq k$ and

$$\sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m}}{|\mathbf{P} - \mathbf{P}'|} = \sum_{\mathbf{P}' \in UC(\mathbf{P})} \sqrt{4\pi} D_L(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m} \right) \Big|_{\ell=0, \kappa \rightarrow 0} \quad (6.100)$$

where the sums are over all atomic sites \mathbf{P}' which are in the same unit cell as \mathbf{P} ; the structure coefficients $D_L(\mathbf{P} - \mathbf{P}', \mathbf{0})$ for $\ell = 0$ and $\kappa \rightarrow 0$ can directly be taken from the ASW program.

All in all the sum Eq. (6.94) is for $i = k$ given by

$$\begin{aligned} \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ii\sigma}^{\mathbf{P}'}}{|\mathbf{P} - \mathbf{P}'|} &= \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m}}{|\mathbf{P} - \mathbf{P}'|} + \frac{1}{m} \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{1}{|\mathbf{P} - \mathbf{P}'|} \\ &= \sum_{\mathbf{P}' \in UC(\mathbf{P})} \sqrt{4\pi} D_L(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m} \right) \Big|_{\ell=0, \kappa \rightarrow 0} + K \end{aligned} \quad (6.101)$$

where we introduced a constant

$$K = \frac{1}{m} \sum_{\mathbf{P}' \neq \mathbf{P}} \frac{1}{|\mathbf{P} - \mathbf{P}'|} \quad (6.102)$$

which does due to the properties of Bravais lattices not depend on \mathbf{P} .

We will see later on that we do not need to calculate K at all.

Altogether we can now write the function $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$ inside S_P as

$$\begin{aligned} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) &= -4\pi \sum_{k=1}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \times \\ &\quad \times \left\{ \frac{1}{(r, \mathbf{P})} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ &\quad \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P}) (\varphi_{i\sigma}^* \varphi_{k\sigma})(r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\ &\quad - \sum_{\substack{k=1 \\ k \neq i}}^{N_\sigma} (\varphi_{i\sigma} \varphi_{k\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} \sqrt{4\pi} D_L(\mathbf{P} - \mathbf{P}', \mathbf{0}) Q_{ik\sigma}^{\mathbf{P}'} \Big|_{\ell=0, \kappa \rightarrow 0} \\ &\quad - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} \sqrt{4\pi} D_L(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m} \right) \Big|_{\ell=0, \kappa \rightarrow 0} \\ &\quad - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K \\ &=: (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) \\ &=: (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K. \end{aligned} \quad (6.103)$$

In the last steps we have defined the notation $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ for the inside S_P spherically symmetric part of the function $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$ and the function $(\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P})$ which is just $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ without the additive term involving the unknown constant K .

As we will see, only this function $(\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P})$ has to be calculated.

Using Eqs. (6.92) / (6.93) to write everything explicitly in terms of the radial functions $R_{i\sigma L}$, the function $(\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P})$ is given by

$$\begin{aligned} &(\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) \\ &= -\frac{1}{4\pi} \sum_{k=1}^{N_\sigma} \sum_L R_{i\sigma L}(r, \mathbf{P}) R_{k\sigma L}^*(r, \mathbf{P}) \times \\ &\quad \times \left\{ \frac{1}{(r, \mathbf{P})} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^2 \sum_{L'} R_{i\sigma L'}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ &\quad \left. + \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P}) \sum_{L'} R_{i\sigma L'}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) \right\} \\ &\quad - \frac{1}{\sqrt{4\pi}} \sum_{k=1}^{N_\sigma} \sum_L R_{i\sigma L}(r, \mathbf{P}) R_{k\sigma L}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ik\sigma}^{\mathbf{P}'} - \frac{1}{m} \delta_{ik} \right) \Big|_{\ell''=0, \kappa \rightarrow 0} \end{aligned} \quad (6.104)$$

where the $Q_{ik\sigma}^{\mathbf{P}'}$ are given by Eq. (6.89) and where m is the number of atomic spheres in a unit cell.

Calculation of the numbers $\bar{u}_{xi\sigma}$

In Eq. (6.103) in the previous part we have already seen how the spherically symmetric part $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) = (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K$ of $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$ can be calculated with exception of the term $(\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K$ involving an unknown real valued constant K .

But then $\bar{u}_{xi\sigma}$, Eq. (6.76), is simply given by

$$\begin{aligned}
 \bar{u}_{xi\sigma} &= \sum_{\mathbf{P}} \int_{S_P} u_{xi\sigma}(\mathbf{r}) |\varphi_{i\sigma}(\mathbf{r})|^2 d\mathbf{r} \\
 &= \sum_{\mathbf{P}} \int_{S_P} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d\mathbf{r} \\
 &= \sum_{\mathbf{P}} \int_{S_P} \left[(\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K \right] d\mathbf{r} \\
 &= \sum_{\mathbf{P}} \int_{S_P} (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) d\mathbf{r} - K \sum_{\mathbf{P}} \int_{S_P} (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) d\mathbf{r} \\
 &= \sum_{\mathbf{P}} 4\pi \int_0^{\bar{P}} (r, \mathbf{P})^2 (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) d(r, \mathbf{P}) - K \cdot 1 \\
 &= \left[4\pi \sum_{\mathbf{P}} \int_0^{\bar{P}} (r, \mathbf{P})^2 (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) d(r, \mathbf{P}) \right] - K \\
 &=: \tilde{\bar{u}}_{xi\sigma} - K
 \end{aligned} \tag{6.105}$$

where we have defined numbers $\tilde{\bar{u}}_{xi\sigma}$ which equal $\bar{u}_{xi\sigma}$ when the term containing the unknown constant K is left away. $\tilde{\bar{u}}_{xi\sigma}$ is given by

$$\tilde{\bar{u}}_{xi\sigma} = 4\pi \sum_{\mathbf{P}} \int_0^{\bar{P}} (r, \mathbf{P})^2 (\widetilde{|\varphi_{i\sigma}|^2 u_{xi\sigma}})(r, \mathbf{P}) d(r, \mathbf{P}). \tag{6.106}$$

Calculation of the numbers $M_{ji\sigma}$

For the calculation of the numbers $M_{ji\sigma}$, Eq. (6.77), we of course assume the spin-density $n_{\sigma}(\mathbf{r})$ to be spherically symmetric inside the atomic spheres, i.e., to be given by

$$n_{\sigma}(\mathbf{r}) = n_{\sigma}(r, \mathbf{P}) \quad \text{for } \mathbf{r} \text{ inside } S_P. \tag{6.107}$$

Moreover we assume the functions $|\varphi_{i\sigma}(\mathbf{r})|^2$ to be spherically symmetric inside the atomic spheres; for \mathbf{r} inside S_P they are then given by

$$|\varphi_{i\sigma}|^2(r, \mathbf{P}) = \frac{1}{4\pi} \sum_L |R_{i\sigma L}(r, \mathbf{P})|^2 \tag{6.108}$$

(cf. Eq. (6.86)).

Then $M_{ji\sigma}$ can be calculated from

$$\begin{aligned}
 M_{ji\sigma} &= \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P}) |\varphi_{i\sigma}|^2(r, \mathbf{P})}{n_{\sigma}(r, \mathbf{P})} d\mathbf{r} \\
 &= \sum_{\mathbf{P}} 4\pi \int_0^{\bar{P}} (r, \mathbf{P})^2 \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P}) |\varphi_{i\sigma}|^2(r, \mathbf{P})}{n_{\sigma}(r, \mathbf{P})} d(r, \mathbf{P}) \\
 &= \frac{1}{4\pi} \sum_{\mathbf{P}} \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_{\sigma}(r, \mathbf{P})} \sum_L |R_{j\sigma L}(r, \mathbf{P})|^2 \sum_{L'} |R_{i\sigma L'}(r, \mathbf{P})|^2 d(r, \mathbf{P}).
 \end{aligned} \tag{6.109}$$

Calculation of the numbers $\bar{V}_{xj\sigma}^S$

We first rewrite the formula Eq. (6.78) for $\bar{V}_{xj\sigma}^S$ using the assumptions that both $|\varphi_{j\sigma}(\mathbf{r})|^2$ and $n_{\sigma}(\mathbf{r})$ are spherically symmetric inside the atomic spheres and our results from the first part for the inside the atomic spheres spherically symmetric parts of the functions $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$. We obtain

$$\begin{aligned}
 \bar{V}_{xj\sigma}^S &= \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} \frac{1}{2} \left((|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + c.c. \right) d\mathbf{r} \\
 &= \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d\mathbf{r} + c.c. \\
 &= \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} \left[(|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) - |\varphi_{i\sigma}|^2(r, \mathbf{P}) \cdot K \right] d\mathbf{r} + c.c. \\
 &= \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{2n_{\sigma}(r, \mathbf{P})} \left[\left(\sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) \right) - n_{\sigma}(r, \mathbf{P}) \cdot K \right] d\mathbf{r} + c.c. \\
 &= \left\{ \left(\sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) d\mathbf{r} \right) - \sum_{\mathbf{P}} \int_{S_P} \frac{1}{2} K |\varphi_{j\sigma}|^2(r, \mathbf{P}) d\mathbf{r} \right\} + c.c. \\
 &= \left\{ \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) d\mathbf{r} + c.c. \right\} - K \\
 &=: \tilde{\bar{V}}_{xj\sigma}^S - K.
 \end{aligned} \tag{6.110}$$

We have in the last step introduced numbers $\tilde{\bar{V}}_{xj\sigma}^S$ which equal $\bar{V}_{xj\sigma}^S$ without the term involving the unknown constant K .

Recalling the relationship Eq. (6.108) we can further simplify the formula for $\tilde{\bar{V}}_{xj\sigma}^S$:

$$\begin{aligned}
& \tilde{V}_{xj\sigma}^S \\
&= \Re \left\{ \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) d\mathbf{r} \right\} \\
&= \Re \left\{ \sum_{\mathbf{P}} 4\pi \int_0^{\bar{P}} (r, \mathbf{P})^2 \frac{|\varphi_{j\sigma}|^2(r, \mathbf{P})}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) d(r, \mathbf{P}) \right\} \\
&= \Re \left\{ \sum_{\mathbf{P}} \int_0^{\bar{P}} (r, \mathbf{P})^2 \frac{\sum_L |R_{j\sigma L}(r, \mathbf{P})|^2}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) d(r, \mathbf{P}) \right\}
\end{aligned} \tag{6.111}$$

where the radial functions $(|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P})$ are given by Eq. (6.104).

Some remarks on the system of linear equations for the numbers

$$\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$$

The system of $N_{\sigma} - 1$ linear equations, Eq. (6.79), which has to be solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$ involves the numbers $\bar{u}_{xi\sigma}$ and $\bar{V}_{xj\sigma}^S$ rather than $\tilde{u}_{xi\sigma}$ and $\tilde{V}_{xj\sigma}^S$.

Since we do not know how to calculate $\bar{u}_{xi\sigma}$ and $\bar{V}_{xj\sigma}^S$ we first replace them on the right hand side of the equations by the tilde-quantities using $\bar{u}_{xi\sigma} = \tilde{u}_{xi\sigma} - K$, Eq. (6.105), $\bar{V}_{xj\sigma}^S = \tilde{V}_{xj\sigma}^S - K$, Eq. (6.110), and our knowledge that K is a real valued constant.

Eq. (6.79) then becomes

$$\begin{aligned}
& \sum_{i=1}^{N_{\sigma}-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) = \tilde{V}_{xj\sigma}^S - \frac{1}{2}(\tilde{u}_{xj\sigma} + \tilde{u}_{xj\sigma}^*), \\
& j = 1, \dots, N_{\sigma} - 1
\end{aligned} \tag{6.112}$$

and this system of $N_{\sigma} - 1$ linear equations can be solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$.

Calculation of the KLI exact exchange potentials $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$

First of all we rewrite the formula Eq. (6.80) for the KLI exact exchange potential functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ using our assumptions that the functions $n_{\sigma}(\mathbf{r})$, $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$, and $|\varphi_{i\sigma}(\mathbf{r})|^2$ are spherically symmetric inside the atomic spheres; we then actually obtain functions $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$ which are themselves spherically symmetric inside the atomic spheres and for \mathbf{r} inside the sphere around \mathbf{P} we can therefore write them as $v_{x\sigma}^{\text{KLI}}(r, \mathbf{P})$.

We have

$$\begin{aligned}
& v_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) \tag{6.113} \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + |\varphi_{i\sigma}|^2(r, \mathbf{P}) (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma}) \right] + c.c. \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + |\varphi_{i\sigma}|^2(r, \mathbf{P}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] + c.c. \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[\widetilde{(|\varphi_{i\sigma}|^2 u_{xi\sigma})}(r, \mathbf{P}) - |\varphi_{i\sigma}|^2(r, \mathbf{P}) \cdot K \right] + c.c. \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[\widetilde{(|\varphi_{i\sigma}|^2 u_{xi\sigma})}(r, \mathbf{P}) + |\varphi_{i\sigma}|^2(r, \mathbf{P}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] + c.c. - K
\end{aligned}$$

with $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xN_\sigma\sigma} + \bar{u}_{xN_\sigma\sigma}^*) = 0$.

We see that our unknown constant K just gives a constant additive contribution to the exact exchange potential.

However, additive constants in the potential functions merely effect a shift of the eigenvalues corresponding to the Kohn-Sham orbitals and can therefore be neglected. That is, as exact exchange potential functions we can use the functions

$$\tilde{v}_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) = v_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) + K \tag{6.114}$$

given by

$$\begin{aligned}
& \tilde{v}_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) \tag{6.115} \\
&= \Re \left\{ \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \widetilde{(|\varphi_{i\sigma}|^2 u_{xi\sigma})}(r, \mathbf{P}) + \frac{1}{4\pi} \sum_L |R_{i\sigma L}(r, \mathbf{P})|^2 \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right\}
\end{aligned}$$

with $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \frac{1}{2}(\bar{u}_{xN_\sigma\sigma} + \bar{u}_{xN_\sigma\sigma}^*) = 0$ and with the radial functions $\widetilde{(|\varphi_{i\sigma}|^2 u_{xi\sigma})}(r, \mathbf{P})$ given by Eq. (6.104).

6.5.2 Second approach

Calculation of the functions $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$

From atomic calculations we found that the assumption that the $\varphi_{i\sigma}^* \varphi_{k\sigma}$ are spherically symmetric changes the calculated eigenvalues significantly. Therefore here we only make the assumption that the function $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$,

$$|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) = -\varphi_{i\sigma}(\mathbf{r}) \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{6.116}$$

(see Eq. (6.81)), is spherically symmetric inside each atomic sphere. The occurring integral is restricted to the atomic sphere containing \mathbf{r} ; contributions from the other spheres are taken into account by the terms which we found in the first approach for this purpose (cf. Eq. (6.103)). The additive term containing the constant K is left away from the start.

Denoting the atomic sphere around site \mathbf{P} by S_P , we first calculate inside S_P the spherically symmetric part of

$$-\varphi_{i\sigma}(\mathbf{r}) \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (6.117)$$

For \mathbf{r} inside S_P we can write the occurring Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$ and $\varphi_{k\sigma}(\mathbf{r})$ in the form

$$\begin{aligned} \varphi_{i\sigma}(\mathbf{r}) &= \sum_L R_{i\sigma L}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \\ \varphi_{k\sigma}(\mathbf{r}) &= \sum_L R_{k\sigma L}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \end{aligned}$$

(cf. Eq. (6.74)); furthermore using the relationship

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \quad (6.118)$$

(cf. Eq. (6.58)) where $\tilde{r}_{<}(\tilde{r}_{>})$ denotes the smaller (greater) of (r, \mathbf{P}) and (r', \mathbf{P}) we obtain

$$\begin{aligned} &-\varphi_{i\sigma}(\mathbf{r}) \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \\ &= - \left(\sum_{L'''} R_{i\sigma L'''}(r, \mathbf{P}) Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) \right) \sum_{k=1}^{N_\sigma} \left(\sum_{L^{IV}} R_{k\sigma L^{IV}}^*(r, \mathbf{P}) Y_{L^{IV}}(\hat{\mathbf{r}}, \mathbf{P}) \right) \times \\ &\times \int_{S_P} \left[\sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \times \right. \\ &\left. \times \left(\sum_L R_{i\sigma L}^*(r', \mathbf{P}) Y_L(\hat{\mathbf{r}}', \mathbf{P}) \right) \left(\sum_{L'} R_{k\sigma L'}(r', \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}', \mathbf{P}) \right) \right] d\mathbf{r}'. \end{aligned}$$

Using the real valued Gaunt integrals, Eq. (6.59), and denoting the radius of the atomic sphere S_P by \bar{P} this can be simplified to

$$\begin{aligned} &- \left(\sum_{L'''} R_{i\sigma L'''}(r, \mathbf{P}) Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) \right) \times \\ &\times \sum_{k=1}^{N_\sigma} \left(\sum_{L^{IV}} R_{k\sigma L^{IV}}^*(r, \mathbf{P}) Y_{L^{IV}}(\hat{\mathbf{r}}, \mathbf{P}) \right) \sum_{LL'L''} \frac{4\pi}{2\ell'' + 1} C_{LL'L''} Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \times \\ &\times \left\{ \int_0^{(r, \mathbf{P})} \frac{(r', \mathbf{P})^{\ell''+2}}{(r, \mathbf{P})^{\ell''+1}} R_{i\sigma L}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ &\left. + \int_{(r, \mathbf{P})}^{\bar{P}} \frac{(r, \mathbf{P})^{\ell''}}{(r', \mathbf{P})^{\ell''-1}} R_{i\sigma L}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) \right\}. \end{aligned}$$

Again using the definition of the real valued Gaunt integrals, Eq. (6.59), and adding the contributions from the other spheres (cf. Eqs. (6.103) / (6.104)) the spherical average $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ of $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$ inside S_P is given by

$$\begin{aligned}
& (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) \\
&= \frac{1}{4\pi} \int |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) d(\hat{\mathbf{r}}, \mathbf{P}) \\
&= - \sum_{LL'L''L'''} C_{LL'L''} C_{L''L'''} \frac{1}{2\ell''+1} R_{i\sigma L'''}(r, \mathbf{P}) \sum_{k=1}^{N_\sigma} R_{k\sigma L^{IV}}^*(r, \mathbf{P}) \times \\
&\quad \times \left\{ \frac{1}{(r, \mathbf{P})^{\ell''+1}} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^{\ell''+2} R_{i\sigma L}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\
&\quad \left. + (r, \mathbf{P})^{\ell''} \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P})^{1-\ell''} R_{i\sigma L}^*(r', \mathbf{P}) R_{k\sigma L'}(r', \mathbf{P}) d(r', \mathbf{P}) \right\} - \\
&\quad - \frac{1}{\sqrt{4\pi}} \sum_{k=1}^{N_\sigma} \sum_L R_{i\sigma L}(r, \mathbf{P}) R_{k\sigma L}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ik\sigma}^{\mathbf{P}'} - \frac{1}{m} \delta_{ik} \right) \Bigg|_{\ell''=0, \kappa \rightarrow 0}.
\end{aligned} \tag{6.119}$$

Calculation of the numbers $\bar{u}_{xi\sigma}$

As we have already calculated in the previous part the inside the atomic spheres spherically symmetric functions $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$, Eq. (6.119), the calculation of $\bar{u}_{xi\sigma}$, Eq. (6.76), is now overwhelmingly easy:

$$\begin{aligned}
\bar{u}_{xi\sigma} &= \int |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) d\mathbf{r} \\
&= \sum_{\mathbf{P}} \int_{S_P} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) d\mathbf{r} \\
&= 4\pi \sum_{\mathbf{P}} \int_0^{\bar{P}} (r, \mathbf{P})^2 (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}).
\end{aligned} \tag{6.120}$$

Calculation of the numbers $M_{ji\sigma}$

Assuming the spin-density $n_\sigma(\mathbf{r})$ to be spherically symmetric inside each atomic sphere and moreover applying Eq. (6.74) to rewrite the Kohn-Sham orbitals, we can rewrite the formula Eq. (6.77) for $M_{ji\sigma}$:

$$\begin{aligned}
& M_{ji\sigma} \\
&= \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} d\mathbf{r} \\
&= \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} \left\{ \times \left(\sum_L R_{j\sigma L}^*(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \right) \left(\sum_{L'} R_{j\sigma L'}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \right) \times \right. \\
&\quad \left. \times \left(\sum_{L''} R_{i\sigma L''}^*(r, \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \right) \left(\sum_{L'''} R_{i\sigma L'''}(r, \mathbf{P}) Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) \right) \right\} d\mathbf{r} \\
&= \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{LL'L''L'''} \left\{ R_{j\sigma L}^*(r, \mathbf{P}) R_{j\sigma L'}(r, \mathbf{P}) R_{i\sigma L''}^*(r, \mathbf{P}) R_{i\sigma L'''}(r, \mathbf{P}) \times \right. \\
&\quad \left. \times Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) \right\} d\mathbf{r}.
\end{aligned}$$

Expanding the product $Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P})$ in terms of real valued spherical harmonics, Eqs. (6.61) / (6.62), and using the definition of the real valued Gaunt integrals, Eq. (6.59), we have

$$\begin{aligned}
 & M_{ji\sigma} \\
 = & \sum_{\mathbf{P}} \int_{S_P} \left[\frac{1}{n_\sigma(r, \mathbf{P})} \sum_{LL'L''L'''} R_{j\sigma L}^*(r, \mathbf{P}) R_{j\sigma L'}(r, \mathbf{P}) R_{i\sigma L''}^*(r, \mathbf{P}) R_{i\sigma L'''}(r, \mathbf{P}) \times \right. \\
 & \quad \left. \times C_{LL'L''L'''} Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \right] d\mathbf{r} \\
 = & \sum_{LL'L''L'''} C_{LL'L''L'''} \times \\
 & \times \sum_{\mathbf{P}} \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} R_{j\sigma L}^*(r, \mathbf{P}) R_{j\sigma L'}(r, \mathbf{P}) R_{i\sigma L''}^*(r, \mathbf{P}) R_{i\sigma L'''}(r, \mathbf{P}) d(r, \mathbf{P}).
 \end{aligned} \tag{6.121}$$

Calculation of the numbers $\bar{V}_{xj\sigma}^S$

To calculate the numbers $\bar{V}_{xj\sigma}^S$, Eq. (6.78), we use the inside each atomic sphere spherically symmetric spin-density, the inside the spheres S_P spherically averaged functions $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ from the first part of this subsection (Eq. (6.119)), Eq. (6.74) to rewrite the Kohn-Sham orbitals $\varphi_{j\sigma}(\mathbf{r})$, and the orthonormality of the real valued spherical harmonics:

$$\begin{aligned}
 & \bar{V}_{xj\sigma}^S \\
 = & \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} (u_{xi\sigma}(\mathbf{r}) + u_{xi\sigma}^*(\mathbf{r})) d\mathbf{r} \\
 = & \Re \left\{ \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) d\mathbf{r} \right\} \\
 = & \Re \left\{ \sum_{\mathbf{P}} \int_{S_P} \left[\frac{1}{n_\sigma(r, \mathbf{P})} \left(\sum_L R_{j\sigma L}^*(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \right) \left(\sum_{L'} R_{j\sigma L'}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \right) \times \right. \right. \\
 & \quad \left. \left. \times \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) \right] d\mathbf{r} \right\} \\
 = & \Re \left\{ \sum_{\mathbf{P}} \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} \sum_L R_{j\sigma L}^*(r, \mathbf{P}) R_{j\sigma L}(r, \mathbf{P}) \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}) \right\}.
 \end{aligned} \tag{6.122}$$

Calculation of the KLI exact exchange potentials $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$

After the system of linear equations, Eq. (6.79), has been solved for the numbers $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$, we can use these, the inside the atomic spheres spherically symmetric spin-density, and the inside the atomic spheres S_P spherically averaged functions $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$, Eq. (6.119), to obtain the KLI exact exchange potential $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$, Eq. (6.80), inside S_P :

$$\begin{aligned}
& v_{x\sigma}^{\text{KLI}}(\mathbf{r}) \tag{6.123} \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} [(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + |\varphi_{i\sigma}(\mathbf{r})|^2 (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})] + c.c. \\
&= \frac{1}{2n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + |\varphi_{i\sigma}(\mathbf{r})|^2 \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] + c.c. \\
&= \Re \left\{ \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + |\varphi_{i\sigma}(\mathbf{r})|^2 \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] \right\}.
\end{aligned}$$

In order to obtain the inside the atomic sphere S_P spherically averaged potential function $v_{x\sigma}^{\text{KLI}}(r, \mathbf{P})$ we rewrite the Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$ using Eq. (6.74) and furthermore use the orthonormality of the real valued spherical harmonics:

$$\begin{aligned}
& v_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) \tag{6.124} \\
&= \frac{1}{4\pi} \int v_{x\sigma}^{\text{KLI}}(\mathbf{r}) d(\hat{\mathbf{r}}, \mathbf{P}) \\
&= \frac{1}{4\pi} \int \Re \left\{ \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[\times \left(\sum_{L'} R_{i\sigma L'}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \right) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] \right\} d(\hat{\mathbf{r}}, \mathbf{P}) \\
&= \Re \left\{ \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} \left[+ \frac{1}{4\pi} \sum_L R_{i\sigma L}^*(r, \mathbf{P}) R_{i\sigma L}(r, \mathbf{P}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] \right\}
\end{aligned}$$

where $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xN_\sigma\sigma} + \bar{u}_{xN_\sigma\sigma}^*) = 0$.

6.6 Weighting factors

In this section we consider the case that some equal Kohn-Sham orbitals occur or that each Kohn-Sham orbital represents several electron states. We assume indices i_1, i_2, \dots, i_z and corresponding numbers $q_{i_k}, k = 1, \dots, z$, such that there are q_{i_k} identical Kohn-Sham orbitals $\varphi_{i_k\sigma}(\mathbf{r}), k = 1, \dots, z$. We collect the indices i with $\varphi_{i\sigma}(\mathbf{r}) = \varphi_{i_k\sigma}(\mathbf{r})$ in groups G_{i_k} so that we have

$$\varphi_{i\sigma}(\mathbf{r}) = \varphi_{i_k\sigma}(\mathbf{r}) \quad \text{for all } i \in G_{i_k}, k = 1, \dots, z. \quad (6.125)$$

How can the KLI formulas, Eqs. (6.49)–(6.54), be calculated in this case?

It is quite obvious that we have

$$u_{xi\sigma}(\mathbf{r}) = u_{xi_k\sigma}(\mathbf{r}) = -\frac{1}{\varphi_{i_k\sigma}^*(\mathbf{r})} \sum_{k'=1}^z q_{i_{k'}} \varphi_{i_{k'}\sigma}^*(\mathbf{r}) \int \frac{\varphi_{i_k\sigma}^*(\mathbf{r}') \varphi_{i_{k'}\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.126)$$

for all $i \in G_{i_k}$,

$$\bar{u}_{xi\sigma} = \bar{u}_{xi_k\sigma} = \int u_{xi_k\sigma}(\mathbf{r}) |\varphi_{i_k\sigma}(\mathbf{r})|^2 d\mathbf{r} \quad (6.127)$$

for all $i \in G_{i_k}$,

$$M_{ji\sigma} = M_{ji_{k'}i_k\sigma} = \int \frac{|\varphi_{i_{k'}\sigma}(\mathbf{r})|^2 |\varphi_{i_k\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} d\mathbf{r} \quad (6.128)$$

for all $i \in G_{i_k}, j \in G_{i_{k'}}$, and

$$\bar{V}_{xj\sigma}^S = \bar{V}_{xi_{k'}\sigma}^S = \int \frac{|\varphi_{i_{k'}\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \sum_{k=1}^z q_{i_k} |\varphi_{i_k\sigma}(\mathbf{r})|^2 \frac{1}{2} (u_{xi_k\sigma}(\mathbf{r}) + u_{xi_k\sigma}^*(\mathbf{r})) d\mathbf{r} \quad (6.129)$$

for all $j \in G_{i_{k'}}$.

Now we consider our system of linear equations, Eq. (6.53):

$$\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) = \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*), \quad (6.130)$$

$j = 1, \dots, N_\sigma - 1.$

As a shorthand notation we denote its solutions $\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*)$ as $x_{i\sigma}$.

The linear equations can now be rewritten as

$$\begin{aligned} \sum_{k=1}^{z-1} \sum_{i \in G_{i_k}} (\delta_{ji} - M_{ji_{k'}i_k\sigma}) x_{i\sigma} &= \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*), \\ \left(\sum_{k=1}^{z-1} \sum_{i \in G_{i_k}} (-M_{ji_{k'}i_k\sigma}) x_{i\sigma} \right) + x_{j\sigma} &= \bar{V}_{xj\sigma}^S - \frac{1}{2} (\bar{u}_{xj\sigma} + \bar{u}_{xj\sigma}^*). \end{aligned}$$

But then, both the term inside the large brackets on the left hand sides and the right hand sides of these equations are identical for all $j \in G_{i_{k'}}$ for the same k' . Consequently all the $x_{j\sigma}$ with $j \in G_{i_{k'}}$ for the same k' are identical; we call them $x_{i_{k'}\sigma}$ and the corresponding $\bar{v}_{xi\sigma}^{\text{KLI}}$ -values $\bar{v}_{xi_{k'}\sigma}^{\text{KLI}}$.

The linear equations can now be further simplified:

$$\left(\sum_{k=1}^{z-1} (-q_{i_k} M_{i_{k'} i_k \sigma}) x_{i_k \sigma} \right) + x_{i_{k'} \sigma} = \bar{V}_{xi_{k'} \sigma}^S - \frac{1}{2} \left(\bar{u}_{xi_{k'} \sigma} + \bar{u}_{xi_{k'} \sigma}^* \right). \quad (6.131)$$

Of course we now only need a system of $z - 1$ linear equations since all equations for $j \in G_{i_{k'}}$ for the same k' are identical and we have to set

$$x_{i_z} = \bar{v}_{xi_z \sigma}^{\text{KLI}} - \frac{1}{2} \left(\bar{u}_{xi_z \sigma} + \bar{u}_{xi_z \sigma}^* \right) = 0. \quad (6.132)$$

In order to make the matrix of the above system of linear equations for the unknowns $x_{i_{k'}\sigma}$, Eq. (6.131), symmetric, one simply has to multiply the equation corresponding to the group $G_{i_{k'}}$ with the weighting factor $q_{i_{k'}}$. The matrix element for position $(i_{k'}, i_k)$ is then given by $-q_{i_k} q_{i_{k'}} M_{i_{k'} i_k \sigma}$ and the right hand side element in line $i_{k'}$ is $\left(\bar{V}_{xi_{k'} \sigma}^S - \frac{1}{2} \left(\bar{u}_{xi_{k'} \sigma} + \bar{u}_{xi_{k'} \sigma}^* \right) \right) \cdot q_{i_{k'}}$.

Finally, we obtain for the KLI exact exchange potentials $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$, Eq. (6.54):

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{k=1}^z q_{i_k} |\varphi_{i_k \sigma}(\mathbf{r})|^2 \left[u_{xi_k \sigma}(\mathbf{r}) + \left(\bar{v}_{xi_k \sigma}^{\text{KLI}} - \bar{u}_{xi_k \sigma} \right) \right] + c.c. \quad (6.133)$$

with

$$\bar{v}_{xi_z \sigma}^{\text{KLI}} - \bar{u}_{xi_z \sigma} = 0. \quad (6.134)$$

7. The exact Slater approach

7.1 A simpler approximation for the exact exchange potential

Before we started with the KLI method, we noticed that it is very helpful to use the exact exchange energy functional

$$E_x[n] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \int \int \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (7.1)$$

as a starting point for the generation of an exchange potential; we explained in section 5.2 why this is so.

Since the corresponding exact exchange potential $v_{x\sigma}(\mathbf{r})$ is then given by

$$v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})} \quad (7.2)$$

we made an attempt to find an ad hoc approximation for $v_{x\sigma}(\mathbf{r})$ by applying the chain rule for functional derivatives to Eq. (7.2). We describe our proceeding in the following:

We noticed that it is easy to form the functional derivative of $E_x[n]$, Eq. (7.1), with respect to some Kohn-Sham orbital $\varphi_{i\alpha}(\mathbf{r}')$:

$$\frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} = - \sum_{j=1}^{N_\alpha} \varphi_{j\alpha}^*(\mathbf{r}') \int \frac{\varphi_{i\alpha}^*(\mathbf{r}''') \varphi_{j\alpha}(\mathbf{r}''')}{|\mathbf{r}' - \mathbf{r}'''|} d\mathbf{r}''' \quad (7.3)$$

(see Eq. (6.14)).

Therefore we applied the chain rule for functional derivatives in the form

$$\frac{\delta E_x[n]}{\delta n_\sigma(\mathbf{r})} = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \frac{\delta E_x[n]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} d\mathbf{r}' + c.c. \quad (7.4)$$

However, we now had to face the problem to find an approximation for $\frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}$ which appears to be very difficult, for how are we supposed to know how one specific Kohn-Sham orbital $\varphi_{i\alpha}(\mathbf{r}')$ is going to respond to some small change in the total spin-density $n_\sigma(\mathbf{r})$?

We tried to split this problem into two less difficult pieces by applying the chain rule for functional derivatives to $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{\sigma}(\mathbf{r})}$ in the form

$$\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{\sigma}(\mathbf{r})} = \sum_{\beta=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma}} \int \frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{k\beta}(\mathbf{r}'')} \frac{\delta n_{k\beta}(\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})} d\mathbf{r}'' \quad (7.5)$$

where we introduced "partial" spin-densities

$$n_{k\beta}(\mathbf{r}) = |\varphi_{k\beta}(\mathbf{r})|^2. \quad (7.6)$$

We can write the Kohn-Sham orbital $\varphi_{k\beta}(\mathbf{r})$ in the form

$$\varphi_{k\beta}(\mathbf{r}) = \sqrt{n_{k\beta}(\mathbf{r})} \exp(i\chi_{k\beta}(\mathbf{r})) \quad (7.7)$$

and we assume that the introduced phase factor $\exp(i\chi_{k\beta}(\mathbf{r}))$ is unchanged to first order by changes in $n_{k\beta}(\mathbf{r})$ and that to first order only the Kohn-Sham orbital $\varphi_{k\beta}(\mathbf{r}')$ responds to changes in $n_{k\beta}(\mathbf{r}'')$.

Then, when $n_{k\beta}(\mathbf{r}'')$ is changed by some small amount $\Delta n_{k\beta}(\mathbf{r}'')$, the corresponding first-order change $\Delta\varphi_{i\alpha}(\mathbf{r}')$ is given by

$$\begin{aligned} \Delta\varphi_{i\alpha}(\mathbf{r}') &= \delta_{\alpha\beta}\delta_{ik} \left(\sqrt{n_{k\beta}(\mathbf{r}') + \Delta n_{k\beta}(\mathbf{r}')} - \sqrt{n_{k\beta}(\mathbf{r}')} \right) \exp(i\chi_{k\beta}(\mathbf{r}')) \\ &= \delta_{\alpha\beta}\delta_{ik} \sqrt{n_{k\beta}(\mathbf{r}')} \left(\sqrt{1 + \frac{\Delta n_{k\beta}(\mathbf{r}')}{n_{k\beta}(\mathbf{r}')}} - 1 \right) \exp(i\chi_{k\beta}(\mathbf{r}')). \end{aligned}$$

Using the power series expansion for $\sqrt{1+x}$,

$$\sqrt{1+x} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots, \quad (7.8)$$

which is valid for $|x| \leq 1$, the first-order change $\Delta\varphi_{i\alpha}(\mathbf{r}')$ is given by

$$\begin{aligned} \Delta\varphi_{i\alpha}(\mathbf{r}') &= \delta_{\alpha\beta}\delta_{ik} \frac{1}{2} \sqrt{n_{k\beta}(\mathbf{r}')} \frac{\Delta n_{k\beta}(\mathbf{r}')}{n_{k\beta}(\mathbf{r}')} \exp(i\chi_{k\beta}(\mathbf{r}')) \\ &= \delta_{\alpha\beta}\delta_{ik} \frac{1}{2n_{k\beta}(\mathbf{r}')} \varphi_{k\beta}(\mathbf{r}') \Delta n_{k\beta}(\mathbf{r}'). \end{aligned} \quad (7.9)$$

Recalling Eq. (4.9) in our section on functional derivation, we see from Eq. (7.9) that $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{k\beta}(\mathbf{r}'')}$ is given by

$$\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{k\beta}(\mathbf{r}'')} = \delta_{\alpha\beta}\delta_{ik} \frac{1}{2n_{k\beta}(\mathbf{r}')} \varphi_{k\beta}(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}''). \quad (7.10)$$

We still have to find an approximation for $\frac{\delta n_{k\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})}$ which also occurs in Eq. (7.5).

From Eq. (7.6) it is clear that we have

$$n_\sigma(\mathbf{r}) = \sum_{k=1}^{N_\sigma} n_{k\sigma}(\mathbf{r}). \quad (7.11)$$

But since it can be seen from the definition of functional derivation, section 4.1, that a sum of functional derivatives with respect to always the same function is just the functional derivative of the sum with respect to this function, we obtain

$$\sum_{k=1}^{N_\sigma} \frac{\delta n_{k\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} = \frac{\delta n_\beta(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} \quad (7.12)$$

and it is quite obvious that

$$\frac{\delta n_\beta(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} = \delta_{\beta\sigma} \delta(\mathbf{r} - \mathbf{r}''). \quad (7.13)$$

By equation (7.11) we are induced to assume that to first order only the $n_{k\sigma}(\mathbf{r}'')$ will respond to a change in $n_\sigma(\mathbf{r})$ and we are looking for approximations to $\frac{\delta n_{k\sigma}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})}$ satisfying

$$\sum_{k=1}^{N_\sigma} \frac{\delta n_{k\sigma}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} = \delta(\mathbf{r} - \mathbf{r}''). \quad (7.14)$$

Due to the theory of functional derivation, section 4.1, the question is how big the first order change $\Delta n_{k\sigma}(\mathbf{r}'')$ in $n_{k\sigma}(\mathbf{r}'')$ will be when $n_\sigma(\mathbf{r})$ is changed by some small amount $\Delta n_\sigma(\mathbf{r})$.

Our intuition suggests that the change $\Delta n_{k\sigma}(\mathbf{r}'')$ will be greater for relatively greater $n_{k\sigma}(\mathbf{r}'')$ and smaller for relatively smaller $n_{k\sigma}(\mathbf{r}'')$.

Therefore we try an ansatz

$$\frac{\delta n_{k\sigma}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} = \gamma \frac{n_{k\sigma}(\mathbf{r}'')}{n_\sigma(\mathbf{r}'')} \delta(\mathbf{r} - \mathbf{r}'') \quad (7.15)$$

with some proportionality constant γ .

Then, from the condition Eq. (7.14) and due to $\sum_{k=1}^{N_\sigma} n_{k\sigma}(\mathbf{r}'') = n_\sigma(\mathbf{r}'')$ we immediately obtain $\gamma = 1$ and hence have

$$\frac{\delta n_{k\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} = \frac{n_{k\sigma}(\mathbf{r}'')}{n_\sigma(\mathbf{r}'')} \delta(\mathbf{r} - \mathbf{r}'') \delta_{\beta\sigma}. \quad (7.16)$$

Inserting our approximations Eqs. (7.10) and (7.16) into Eq. (7.5) we obtain an approximation for $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{\sigma}(\mathbf{r})}$:

$$\begin{aligned}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{\sigma}(\mathbf{r})} &= \sum_{\beta=\uparrow,\downarrow} \sum_{k=1}^{N_{\sigma}} \int \delta_{\alpha\beta} \delta_{ik} \frac{1}{2n_{k\beta}(\mathbf{r}')} \varphi_{k\beta}(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') \times \\ &\quad \times \frac{n_{k\sigma}(\mathbf{r}'')}{n_{\sigma}(\mathbf{r}'')} \delta(\mathbf{r} - \mathbf{r}'') \delta_{\beta\sigma} d\mathbf{r}'' \\ &= \frac{1}{2n_{\sigma}(\mathbf{r}')} \varphi_{i\sigma}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \delta_{\alpha\sigma}.\end{aligned}\quad (7.17)$$

Now in addition using Eqs. (7.4) and (7.3) we get an approximation for the exact exchange potential $v_{x\sigma}(\mathbf{r})$:

$$\begin{aligned}v_{x\sigma}(\mathbf{r}) &= \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_{\alpha}} \int \left(- \sum_{j=1}^{N_{\alpha}} \varphi_{j\alpha}^*(\mathbf{r}') \int \frac{\varphi_{i\alpha}^*(\mathbf{r}''') \varphi_{j\alpha}(\mathbf{r}''')}{|\mathbf{r}' - \mathbf{r}'''|} d\mathbf{r}''' \right) \times \\ &\quad \times \frac{1}{2n_{\sigma}(\mathbf{r}')} \varphi_{i\sigma}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \delta_{\alpha\sigma} d\mathbf{r}' + c.c. \\ &= - \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''|} d\mathbf{r}''' \right) \frac{1}{2n_{\sigma}(\mathbf{r})} \varphi_{i\sigma}(\mathbf{r}) + c.c. \\ &= - \frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''|} d\mathbf{r}''' \right) + c.c.\end{aligned}\quad (7.18)$$

Of course, our approximations for $\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta n_{k\beta}(\mathbf{r}'')}$, Eq. (7.10), and for $\frac{\delta n_{k\beta}(\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})}$, Eq. (7.16), which we made during the derivation of our formula (7.18) for the exact exchange potential are very questionable.

However, it is interesting that one just gets the exact Slater exchange potential which first appears in Eq. (7) of Ref. [26].

As we already saw in section 6.1 and as was shown by Sharp and Horton in Ref. [110] this exact Slater exchange potential can be regarded as an approximation to the OEP potential corresponding to the exact exchange energy.

Consequently it provides some justification for our approximations Eqs. (7.10) and (7.16).

But at the end of section 6.1 we also noted that compared with the KLI approximation this exact Slater exchange potential is a somewhat poorer approximation to the OEP potential corresponding to the exact exchange energy.

Nevertheless, the exact Slater exchange potential can be calculated more straightforwardly and it exhibits the correct $-\frac{1}{r}$ limiting behavior for $r \rightarrow \infty$ as can be seen exactly as in the case of the KLI exchange potential, Eqs. (6.42) ff.

We therefore present in sections 7.2 and 7.3 how the exact Slater exchange potential, Eq. (7.18), can be incorporated into our program for atomic calculations and into our augmented spherical waves (ASW) program, respectively.

Furthermore, in section 8.1 we compare exact Slater exchange potentials with KLI exact exchange potentials; both potentials were calculated with the help of our program for atomic calculations.

7.2 Using the Slater exchange potential for atomic calculations

In the present section we describe how the exact Slater exchange potential

$$v_{x\sigma}^{\text{Sla}}(\mathbf{r}) = -\frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''} d\mathbf{r}''' \right) + c.c. \quad (7.19)$$

(see Eq. (7.18)) can be calculated in the framework of a program for atomic calculations.

To do this, we again use the notational concepts introduced in section 6.4:

$$i = (n, \ell, m_{\ell}) \quad (7.20)$$

$$j = (n'', \ell'', m_{\ell''}), \quad (7.21)$$

$$\varphi_{i\sigma}(\mathbf{r}) = R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}). \quad (7.22)$$

We start by rewriting the integral term in Eq. (7.19),

$$\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''} d\mathbf{r}'''. \quad (7.23)$$

Writing the Kohn-Sham orbitals in the numerator of the integrand as products of their radial and angular parts, Eq. (7.22), and applying

$$\frac{1}{|\mathbf{r} - \mathbf{r}'''} = \sum_{L'} \frac{4\pi}{2\ell' + 1} \frac{\tilde{r}_{<}^{\ell'}}{\tilde{r}_{>}^{\ell'+1}} Y_{L'}(\hat{\mathbf{r}}''') Y_{L'}(\hat{\mathbf{r}}) \quad (7.24)$$

where $\tilde{r}_{<} (\tilde{r}_{>})$ denotes the smaller (greater) of r and r''' (see Eq. (6.58)) we obtain

$$\begin{aligned} & \int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''} d\mathbf{r}''' \quad (7.25) \\ &= \int R_{n\ell\sigma}^*(r''') Y_L(\hat{\mathbf{r}}''') R_{n''\ell''\sigma}(r''') Y_{L''}(\hat{\mathbf{r}}''') \sum_{L'} \frac{4\pi}{2\ell' + 1} \frac{\tilde{r}_{<}^{\ell'}}{\tilde{r}_{>}^{\ell'+1}} Y_{L'}(\hat{\mathbf{r}}''') Y_{L'}(\hat{\mathbf{r}}) d\mathbf{r}''' \\ &= \sum_{L'} C_{LL'L''} \frac{4\pi}{2\ell' + 1} \int_0^{\infty} (r''')^2 \frac{\tilde{r}_{<}^{\ell'}}{\tilde{r}_{>}^{\ell'+1}} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' Y_{L'}(\hat{\mathbf{r}}) \\ &= \sum_{L'} C_{LL'L''} \frac{4\pi}{2\ell' + 1} \left\{ \frac{1}{r^{\ell'+1}} \int_0^r (r''')^{\ell'+2} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' + \right. \\ & \quad \left. + r^{\ell'} \int_r^{\infty} (r''')^{1-\ell'} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' \right\} Y_{L'}(\hat{\mathbf{r}}) \end{aligned}$$

where in the second step we used the definition of the Gaunt integrals $C_{LL'L''}$, Eq. (6.59).

Now coming back to the complete formula for $v_{x\sigma}^{\text{Sla}}(\mathbf{r})$, Eq. (7.19), and assuming the spin-density $n_\sigma(\mathbf{r})$ to be spherically symmetric, i.e., to be given by $n_\sigma(r)$ we can write

$$v_{x\sigma}^{\text{Sla}}(\mathbf{r}) = -\frac{1}{2n_\sigma(r)} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} R_{n''\ell''\sigma}^*(r) Y_{L''}(\hat{\mathbf{r}}) R_{n\ell\sigma}(r) Y_L(\hat{\mathbf{r}}) \sum_{L'} C_{LL'L''} \frac{4\pi}{2\ell'+1} \times \\ \times \left\{ \frac{1}{r^{\ell'+1}} \int_0^r (r''')^{\ell'+2} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' + \right. \\ \left. + r^{\ell'} \int_r^\infty (r''')^{1-\ell'} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' \right\} Y_{L'}(\hat{\mathbf{r}}) + c.c. \quad (7.26)$$

We are interested in the spherically symmetric part $v_{x\sigma}^{\text{Sla}}(r)$ of $v_{x\sigma}^{\text{Sla}}(\mathbf{r})$; this is given by

$$v_{x\sigma}^{\text{Sla}}(r) = \frac{1}{4\pi} \int v_{x\sigma}^{\text{Sla}}(\mathbf{r}) d\hat{\mathbf{r}} \quad (7.27)$$

and hence, again using the definition of the Gaunt integrals, Eq. (6.59), by

$$v_{x\sigma}^{\text{Sla}}(r) = -\frac{1}{2n_\sigma(r)} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} R_{n''\ell''\sigma}^*(r) R_{n\ell\sigma}(r) \sum_{L'} (C_{LL'L''})^2 \frac{1}{2\ell'+1} \times \\ \times \left\{ \frac{1}{r^{\ell'+1}} \int_0^r (r''')^{\ell'+2} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' + \right. \\ \left. + r^{\ell'} \int_r^\infty (r''')^{1-\ell'} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' \right\} + c.c. \\ = -\frac{1}{n_\sigma(r)} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} R_{n''\ell''\sigma}^*(r) R_{n\ell\sigma}(r) \sum_{L'} (C_{LL'L''})^2 \frac{1}{2\ell'+1} \times \\ \times \left\{ \frac{1}{r^{\ell'+1}} \int_0^r (r''')^{\ell'+2} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' + \right. \\ \left. + r^{\ell'} \int_r^\infty (r''')^{1-\ell'} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' \right\}. \quad (7.28)$$

Eq. (7.28) is a formula which allows us the straightforward calculation of the exact Slater exchange potential.

7.3 Using the Slater exchange potential in the augmented spherical waves (ASW) program

In the present section we want to see how the exact Slater exchange potential

$$v_{x\sigma}^{\text{Sla}}(\mathbf{r}) = -\frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''} d\mathbf{r}''' \right) + c.c., \quad (7.29)$$

Eq. (7.18), can be calculated in the augmented spherical waves (ASW) program whose characteristic features we outlined at the beginning of section 6.5.

The first important thing we note is that the part

$$-\sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''} d\mathbf{r}''' \right) \quad (7.30)$$

of the formula (7.29) for the exact Slater exchange potential is exactly the same as the expression

$$|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) \quad (7.31)$$

the calculation of which we described in subsections 6.5.1 and 6.5.2.

In the first approach we saw that for \mathbf{r} inside the atomic sphere around site \mathbf{P} this function is approximately given by

$$|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) = \left(|\varphi_{i\sigma}|^2 u_{xi\sigma} \right)(r, \mathbf{P}) - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K \quad (7.32)$$

(see Eq. (6.103)) where K is an unknown real valued constant and $\left(|\varphi_{i\sigma}|^2 u_{xi\sigma} \right)(r, \mathbf{P})$ can be calculated from Eq. (6.104).

When we now furthermore assume the spin-density $n_{\sigma}(\mathbf{r})$ to be spherically symmetric inside the atomic spheres, i.e., to be given by a function

$$n_{\sigma}(r, \mathbf{P}) \quad \text{for } \mathbf{r} \text{ inside the atomic sphere } S_P \text{ around site } \mathbf{P}, \quad (7.33)$$

we obtain for \mathbf{r} inside S_P the exact Slater exchange potential, Eq. (7.29), as

$$\begin{aligned} v_{x\sigma}^{\text{Sla}}(r, \mathbf{P}) &= \frac{1}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} \left[\left(|\varphi_{i\sigma}|^2 u_{xi\sigma} \right)(r, \mathbf{P}) - (\varphi_{i\sigma} \varphi_{i\sigma}^*)(r, \mathbf{P}) \cdot K \right] + c.c. \\ &= \left[\frac{1}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} \left(|\varphi_{i\sigma}|^2 u_{xi\sigma} \right)(r, \mathbf{P}) + c.c. \right] - \left[\frac{1}{2n_{\sigma}(r, \mathbf{P})} n_{\sigma}(r, \mathbf{P}) \cdot K + c.c. \right] \\ &= \left[\frac{1}{2n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} \left(|\varphi_{i\sigma}|^2 u_{xi\sigma} \right)(r, \mathbf{P}) + c.c. \right] - K. \end{aligned} \quad (7.34)$$

As in the case of the KLI exact exchange potential, Eq. (6.113), the unknown constant K simply gives a constant additive contribution to the exact exchange potential.

Since additive constants in the potential functions merely effect a shift of the Kohn-Sham eigenvalues by that constant, they can be left away.

Therefore, instead of $v_{x\sigma}^{\text{Sla}}(r, \mathbf{P})$ we can use as exact Slater exchange potentials the functions

$$\tilde{v}_{x\sigma}^{\text{Sla}}(r, \mathbf{P}) = v_{x\sigma}^{\text{Sla}}(r, \mathbf{P}) + K \quad (7.35)$$

given by

$$\tilde{v}_{x\sigma}^{\text{Sla}}(r, \mathbf{P}) = \Re \left\{ \frac{1}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P}) \right\} \quad (7.36)$$

with the functions $(|\varphi_{i\sigma}|^2 \widetilde{u_{xi\sigma}})(r, \mathbf{P})$ given by Eq. (6.104).

Similarly, in the second approach the exact Slater exchange potentials can be calculated from

$$v_{x\sigma}^{\text{Sla}}(r, \mathbf{P}) = \Re \left\{ \frac{1}{n_{\sigma}(r, \mathbf{P})} \sum_{i=1}^{N_{\sigma}} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) \right\} \quad (7.37)$$

where the functions $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ are given by Eq. (6.119).

8. Results

8.1 Atoms

In the present section we compare the exchange potential functions which are obtained in atomic calculations by using the KLI approximation and the exact Slater approach, respectively.

We also present the functions $r v_{x\sigma}^{\text{KLI/Sl}}(r)$ which are found to approach -1 for $r \rightarrow \infty$ reflecting the asymptotic $-\frac{1}{r}$ behavior of the exchange potential functions $v_{x\sigma}^{\text{KLI/Sl}}(r)$. We have already in section 6.2 recognized this asymptotic behavior to be important and we have also already noticed it to be a characteristic feature of both the KLI exact exchange potential and of the exact Slater exchange potential.

The formula for the total KLI exchange potential,

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 \left[(u_{xi\sigma}(\mathbf{r}) + (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})) + c.c. \right] \quad (8.1)$$

(Eq. (6.54)), also suggests a splitting up of the KLI exchange potential into contributions corresponding to the separate Kohn-Sham indices i , namely into the contributions

$$v_{x\sigma i}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_{\sigma}(\mathbf{r})} |\varphi_{i\sigma}(\mathbf{r})|^2 \left[(u_{xi\sigma}(\mathbf{r}) + (\bar{v}_{xi\sigma}^{\text{KLI}} - \bar{u}_{xi\sigma})) + c.c. \right] \quad (8.2)$$

which satisfy

$$\sum_{i=1}^{N_{\sigma}} v_{x\sigma i}^{\text{KLI}}(\mathbf{r}) = v_{x\sigma}^{\text{KLI}}(\mathbf{r}) \quad (8.3)$$

and which are in the atomic case given by

$$v_{x\sigma i}^{\text{KLI}}(r) = \frac{1}{8\pi n_{\sigma}(r)} R_{n\ell\sigma}(r) \left((\varphi^* u_x)_{i\sigma L}(r) + R_{n\ell\sigma}^*(r) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right) + c.c. \quad (8.4)$$

(cf. Eq. (6.71)).

The corresponding additive components of the exact Slater exchange potential are found to be

$$v_{x\sigma i}^{\text{Sla}}(\mathbf{r}) = -\frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \left(\int \frac{\varphi_{i\sigma}^*(\mathbf{r}''') \varphi_{j\sigma}(\mathbf{r}''')}{|\mathbf{r} - \mathbf{r}'''|} d\mathbf{r}''' \right) + c.c. \quad (8.5)$$

(cf. Eq. (7.19)) and in particular, in the atomic context,

$$\begin{aligned} v_{x\sigma i}^{\text{Sla}}(r) = & -\frac{1}{n_{\sigma}(r)} \sum_{j=1}^{N_{\sigma}} R_{n''\ell''\sigma}^*(r) R_{n\ell\sigma}(r) \sum_{L'} (C_{LL'L''})^2 \frac{1}{2\ell' + 1} \times \\ & \times \left\{ \frac{1}{r^{\ell'+1}} \int_0^r (r''')^{\ell'+2} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' + \right. \\ & \left. + r^{\ell'} \int_r^{\infty} (r''')^{1-\ell'} R_{n\ell\sigma}^*(r''') R_{n''\ell''\sigma}(r''') dr''' \right\} \end{aligned} \quad (8.6)$$

(cf. Eq. (7.28)).

Therefore, we also compare the additive components $v_{x\sigma i}^{\text{KLI}}(r)$ with $v_{x\sigma i}^{\text{Sla}}(r)$, at least for some of the smaller atoms.

Furthermore we give the products $rv_{x\sigma i}^{\text{KLI}}(r)$ and $rv_{x\sigma i}^{\text{Sla}}(r)$. There we find the asymptotic $-\frac{1}{r}$ behavior of both $v_{x\sigma}^{\text{KLI}}(r)$ and $v_{x\sigma}^{\text{Sla}}(r)$ to be brought about by the highest occupied spin-orbital contributions. This manifests itself in

$$rv_{x\sigma i}^{\text{KLI/Sla}}(r) \rightarrow -\frac{1}{m} \quad \text{for } r \rightarrow \infty \quad (8.7)$$

whenever i is one of the m degenerate highest occupied Kohn-Sham spin-orbital indices.

Finally, we also present the KLI and the exact Slater results obtained for the highest occupied energy eigenvalues for each spin and the total energy results and compare them with each other and with the spin-unrestricted Hartree-Fock (SUHF) results given in Ref. [111].

As we already foretold in section 6.3, the KLI results for the total energy and for the highest occupied spin-orbital eigenvalues closely approximate the SUHF results for these values.

For our comparisons we chose six atoms, the alkali Li, Be as an atom where the last filled subshell is an s subshell, N and P as atoms with incomplete p subshell, the halogen Cl, and the noble gas atom Ar.

Atomic units are used throughout and in all our figures we use a logarithmic scale for the r -axis.

All figures are given on the following pages 78–94. In Figs. 8.1 to 8.10 we show the total exchange potential functions for the six atoms; we use separate figures for the spin-up and the spin-down potentials but present in each figure both the KLI (continuous lines) and the exact Slater result (dashed lines). For Be and Ar only one figure is given since the spin-up and spin-down results are identical.

Figs. 8.11 to 8.20 compare the KLI and exact Slater exchange potential functions multiplied with r . They show the correct asymptotic behavior

$$rv_{x\sigma}(r) \rightarrow -1 \quad \text{as} \quad r \rightarrow \infty \quad (8.8)$$

for both KLI and exact Slater approach.

Finally, Figs. 8.21 to 8.30 show the additive components $v_{x\sigma i}(r)$ and $rv_{x\sigma i}(r)$ of $v_{x\sigma}(r)$ and $rv_{x\sigma}(r)$ for Li, Be, and N.

We see from the figures that the KLI and the exact Slater functions have a rather similar shape in principle but their function values often differ considerably even at moderately large radii r .

The comparison of the KLI and Slater exchange potential with other methods is given in the following section.

(The text continues on page 95.)

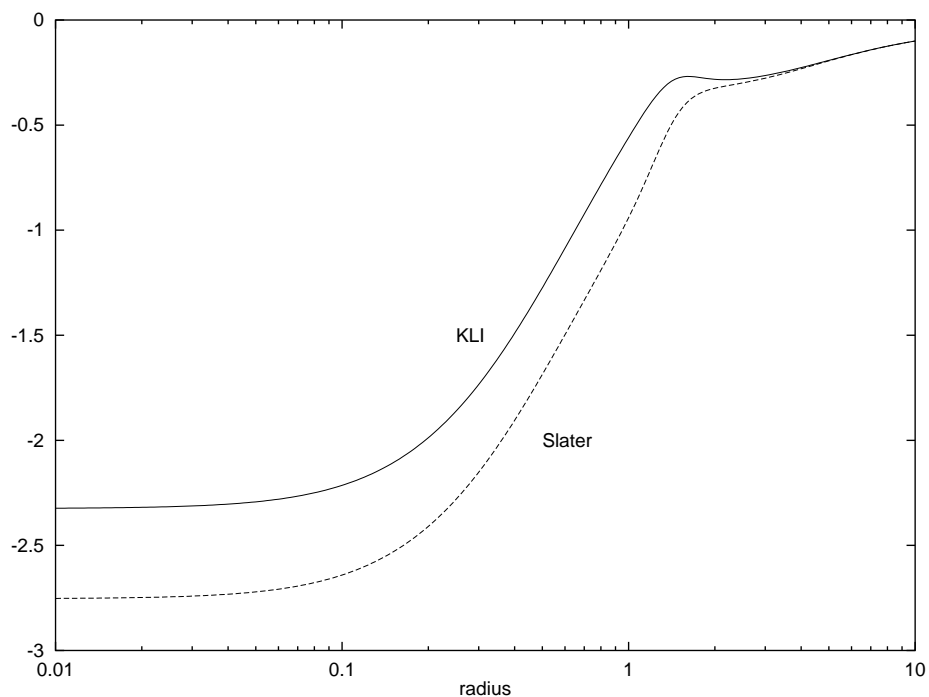


Fig. 8.1: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for Li. Atomic units are used and the r -axis is scaled logarithmically.

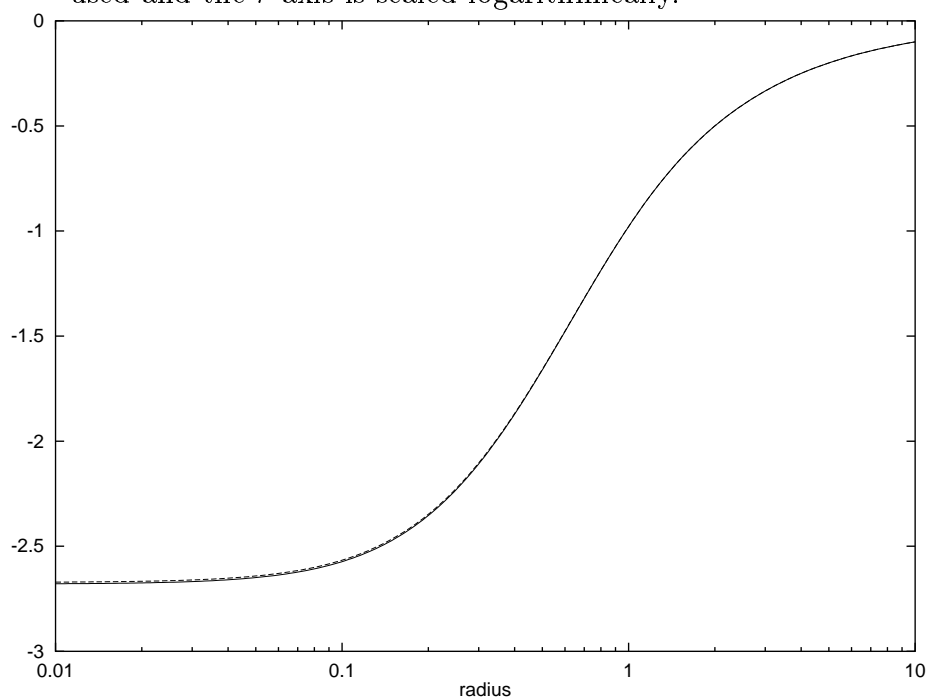


Fig. 8.2: KLI and exact Slater spin-down exchange potential functions, $v_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\downarrow}^{\text{Slat}}(r)$ (dashed line), for Li. Atomic units are used and the r -axis is scaled logarithmically.

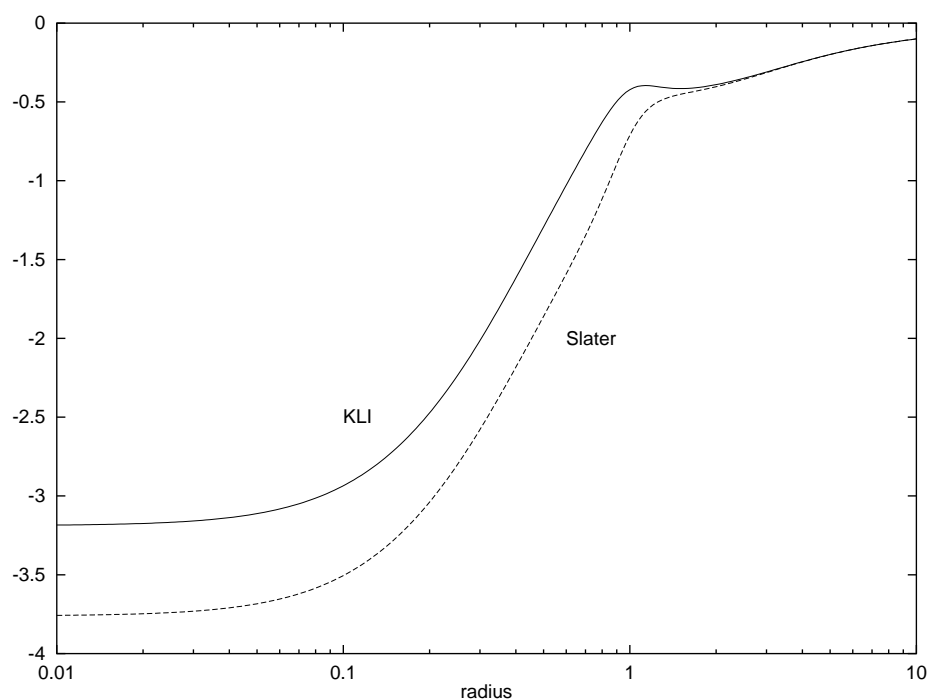


Fig. 8.3: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Sl}}(r)$ (dashed line), for Be (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

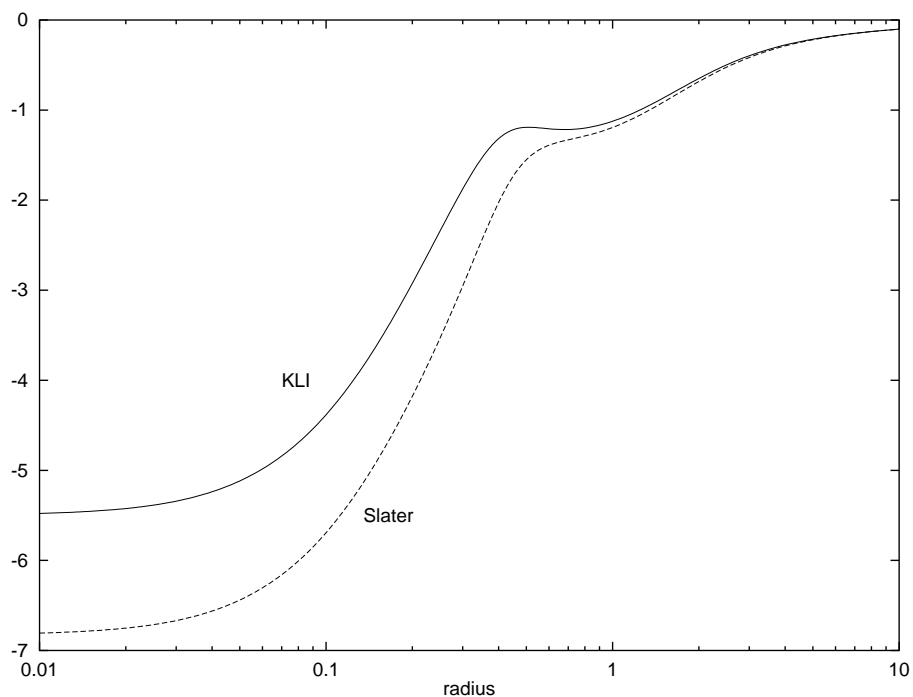


Fig. 8.4: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for N. Atomic units are used and the r -axis is scaled logarithmically.

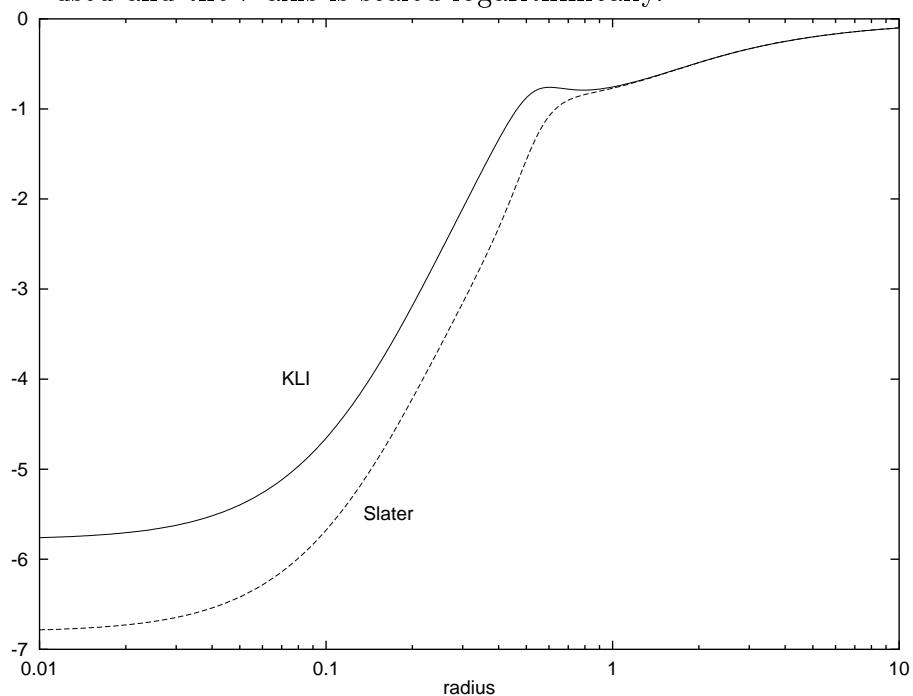


Fig. 8.5: KLI and exact Slater spin-down exchange potential functions, $v_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\downarrow}^{\text{Slat}}(r)$ (dashed line), for N. Atomic units are used and the r -axis is scaled logarithmically.

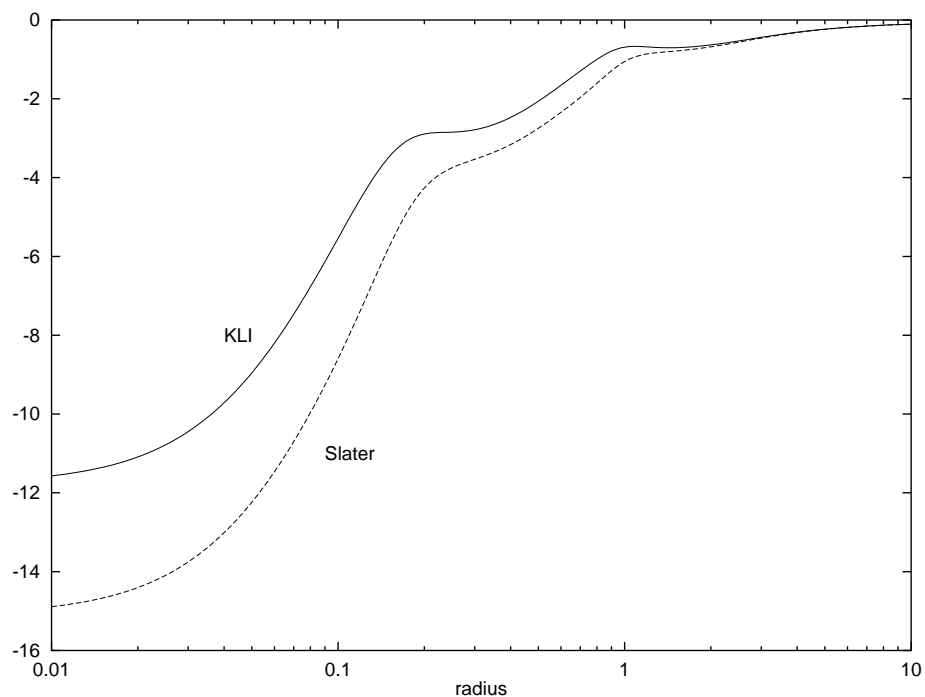


Fig. 8.6: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Slater}}(r)$ (dashed line), for P. Atomic units are used and the r -axis is scaled logarithmically.

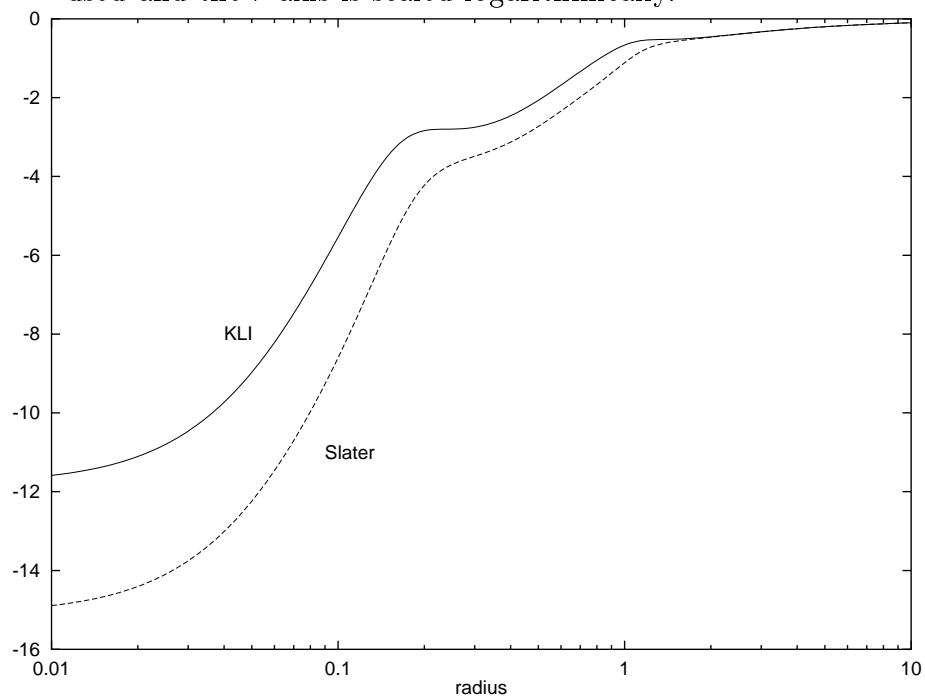


Fig. 8.7: KLI and exact Slater spin-down exchange potential functions, $v_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\downarrow}^{\text{Slater}}(r)$ (dashed line), for P. Atomic units are used and the r -axis is scaled logarithmically.

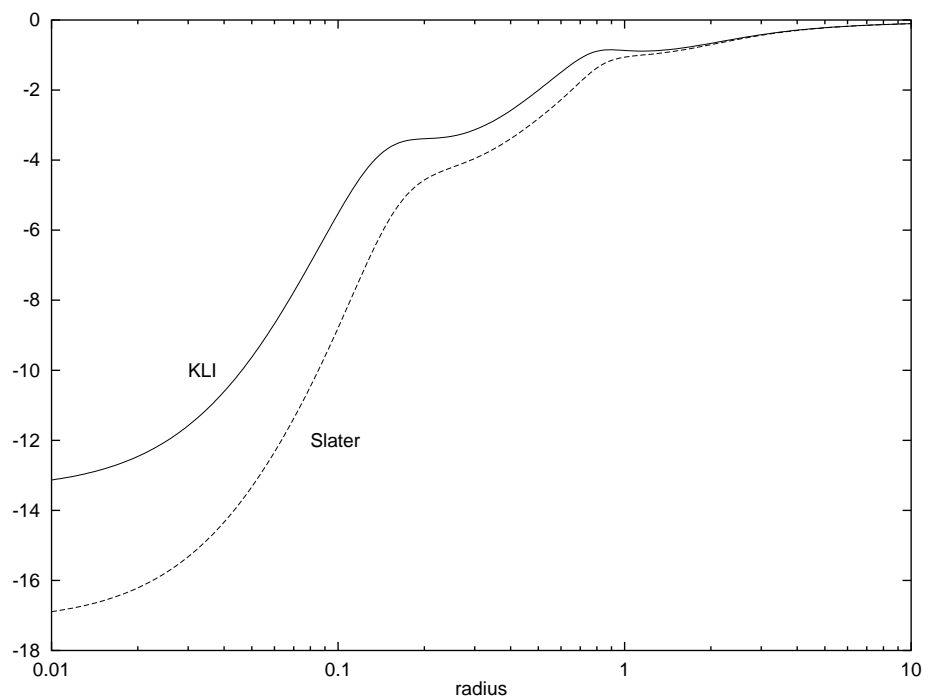


Fig. 8.8: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for Cl. Atomic units are used and the r -axis is scaled logarithmically.

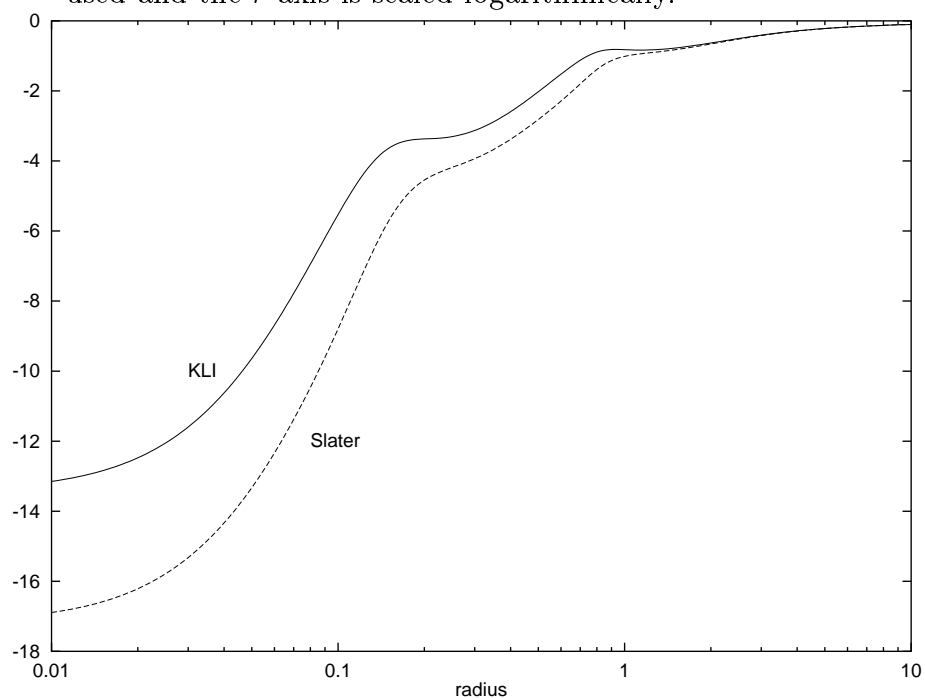


Fig. 8.9: KLI and exact Slater spin-down exchange potential functions, $v_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\downarrow}^{\text{Slat}}(r)$ (dashed line), for Cl. Atomic units are used and the r -axis is scaled logarithmically.

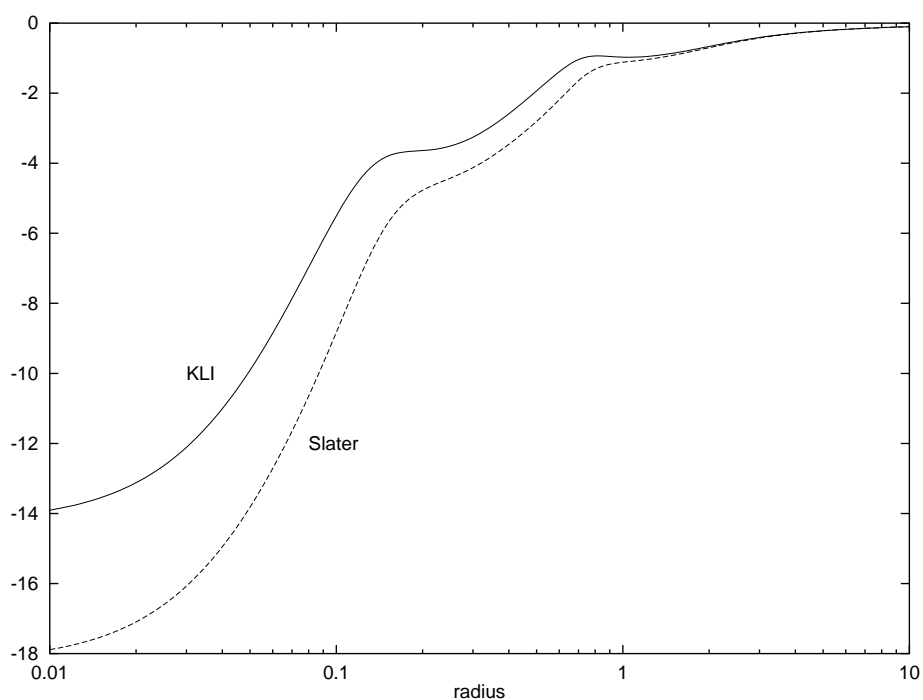


Fig. 8.10: KLI and exact Slater spin-up exchange potential functions, $v_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $v_{x\uparrow}^{\text{Slater}}(r)$ (dashed line), for Ar (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

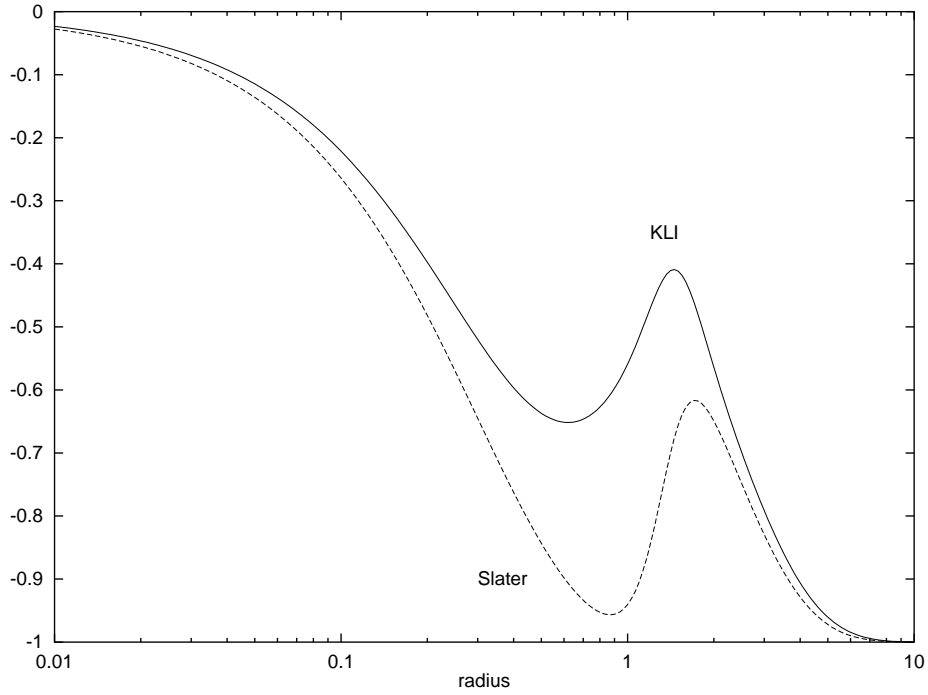


Fig. 8.11: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for Li. Atomic units are used and the r -axis is scaled logarithmically.

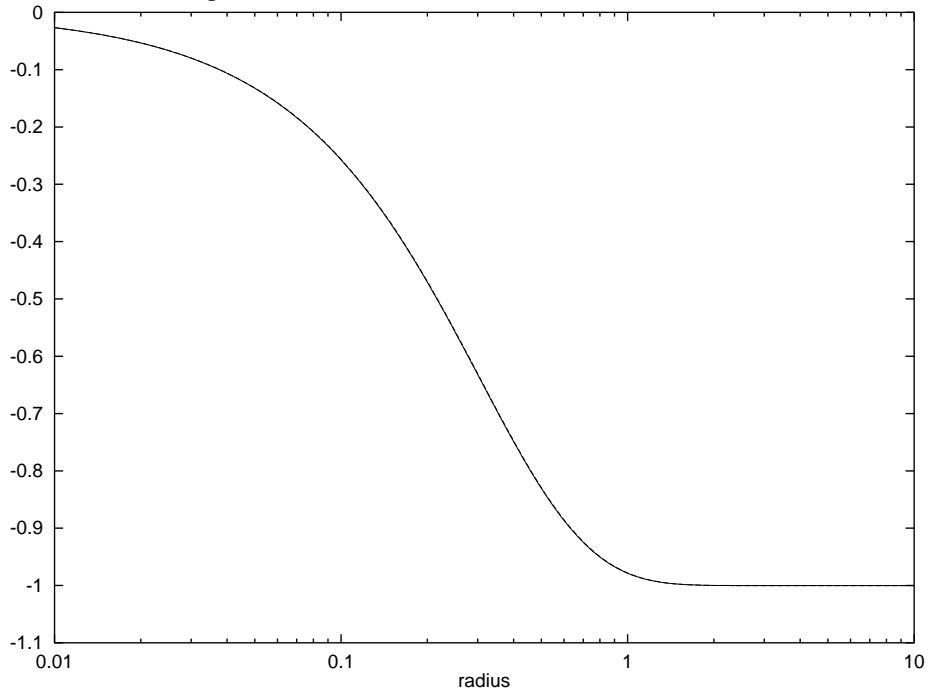


Fig. 8.12: KLI and exact Slater spin-down exchange potential functions multiplied with the radius, $rv_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\downarrow}^{\text{Slat}}(r)$ (dashed line), for Li. Atomic units are used and the r -axis is scaled logarithmically.

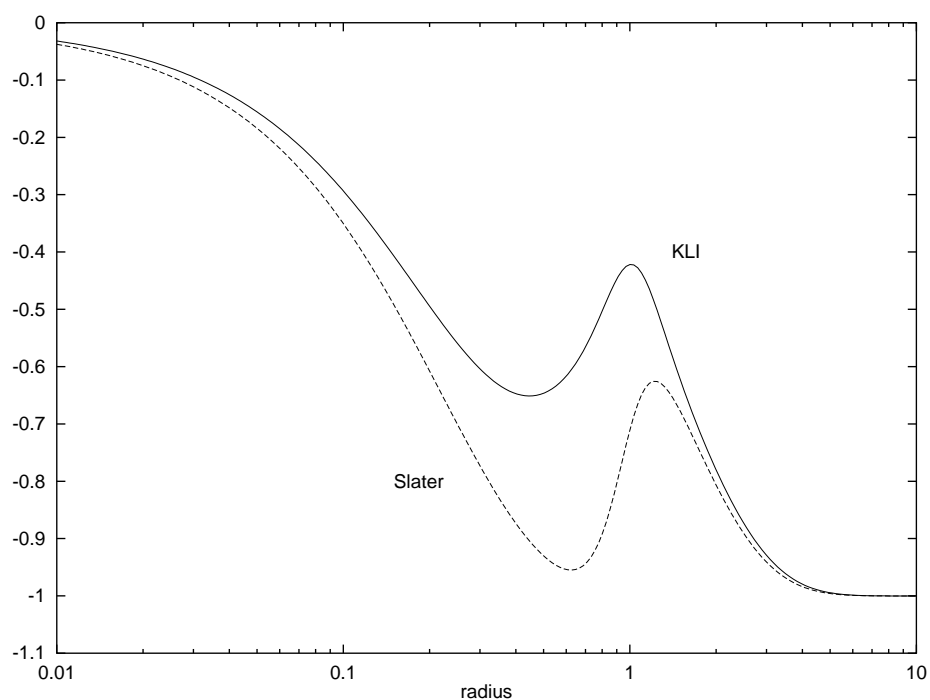


Fig. 8.13: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Sla}}(r)$ (dashed line), for Be (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

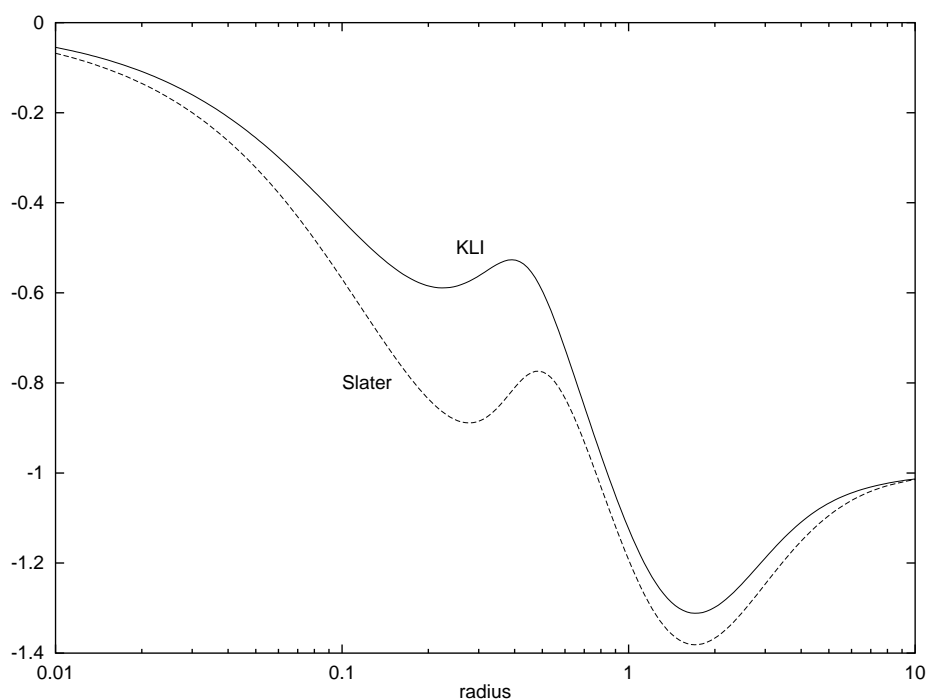


Fig. 8.14: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for N. Atomic units are used and the r -axis is scaled logarithmically.

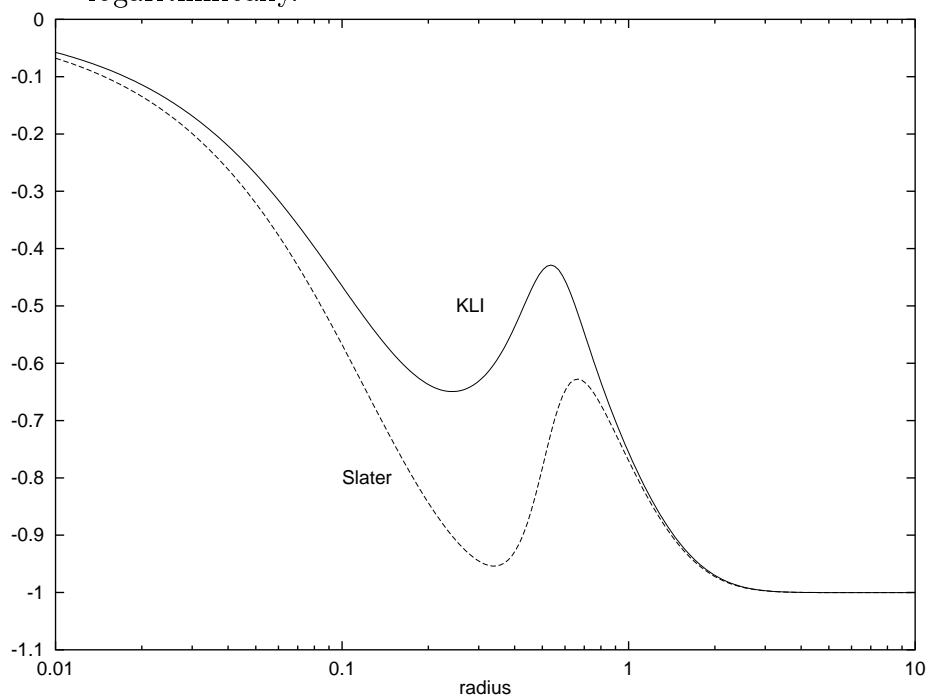


Fig. 8.15: KLI and exact Slater spin-down exchange potential functions multiplied with the radius, $rv_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\downarrow}^{\text{Slat}}(r)$ (dashed line), for N. Atomic units are used and the r -axis is scaled logarithmically.

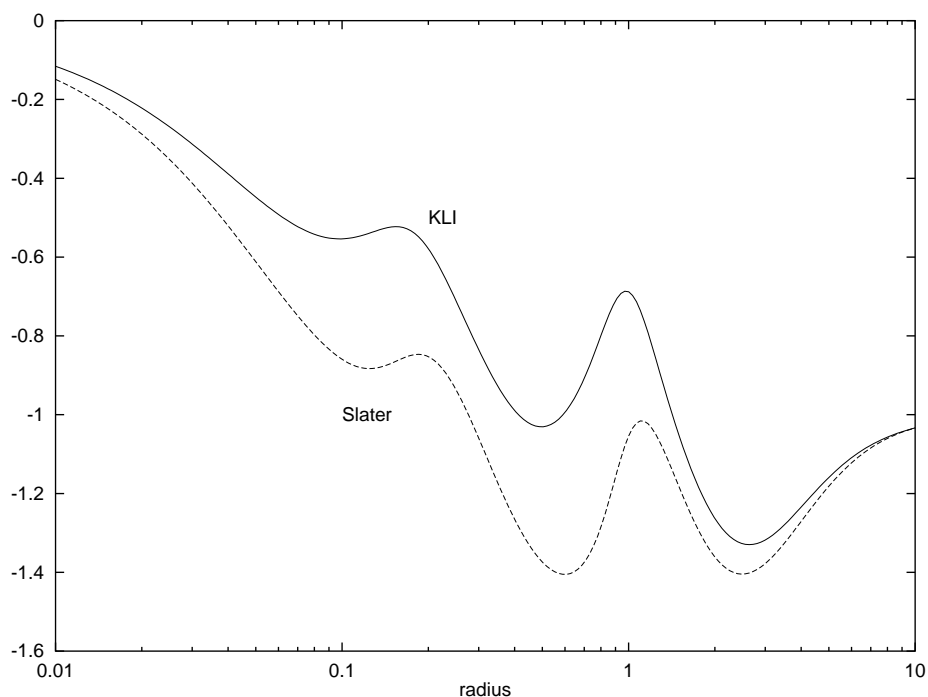


Fig. 8.16: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Slater}}(r)$ (dashed line), for P. Atomic units are used and the r -axis is scaled logarithmically.

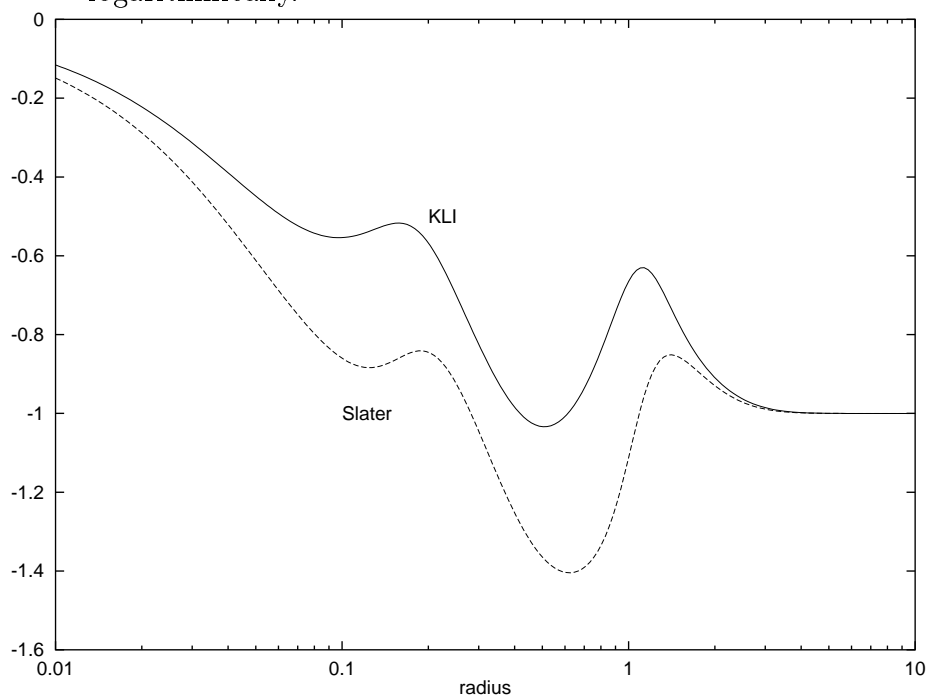


Fig. 8.17: KLI and exact Slater spin-down exchange potential functions multiplied with the radius, $rv_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\downarrow}^{\text{Slater}}(r)$ (dashed line), for P. Atomic units are used and the r -axis is scaled logarithmically.

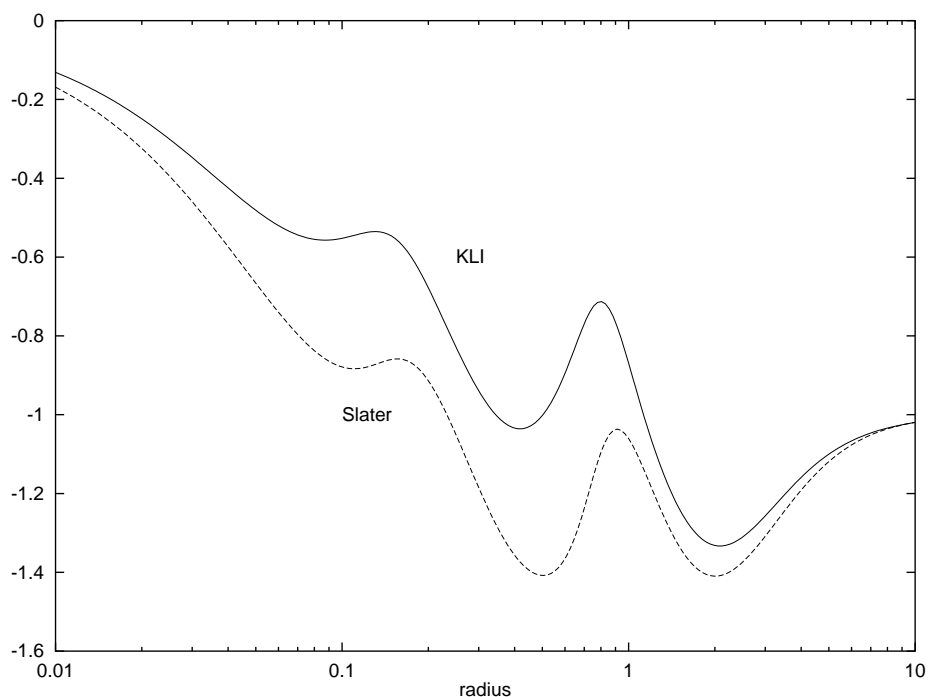


Fig. 8.18: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Slater}}(r)$ (dashed line), for Cl. Atomic units are used and the r -axis is scaled logarithmically.

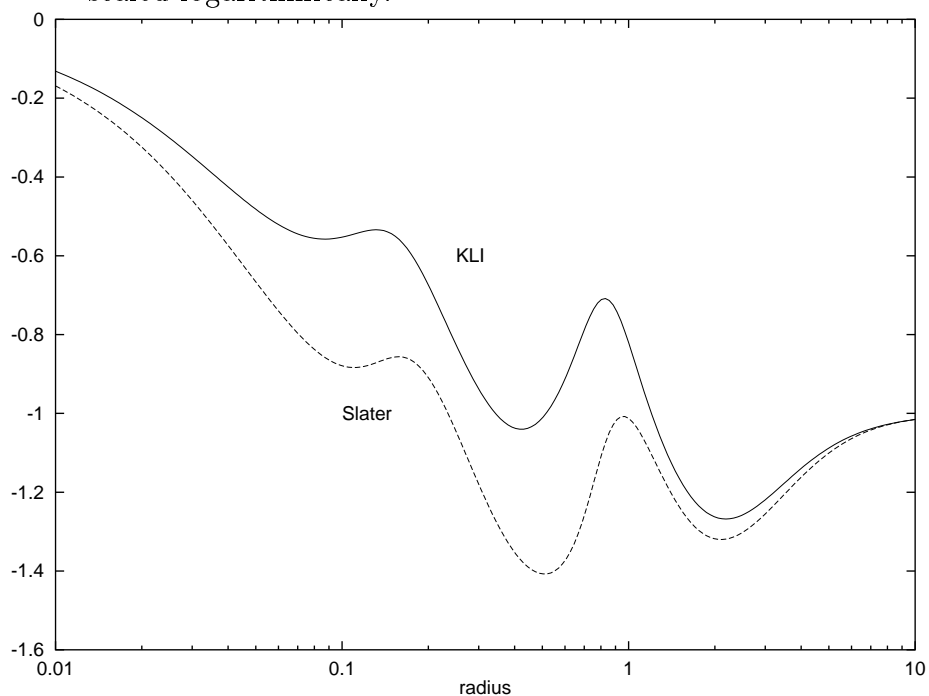


Fig. 8.19: KLI and exact Slater spin-down exchange potential functions multiplied with the radius, $rv_{x\downarrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\downarrow}^{\text{Slater}}(r)$ (dashed line), for Cl. Atomic units are used and the r -axis is scaled logarithmically.

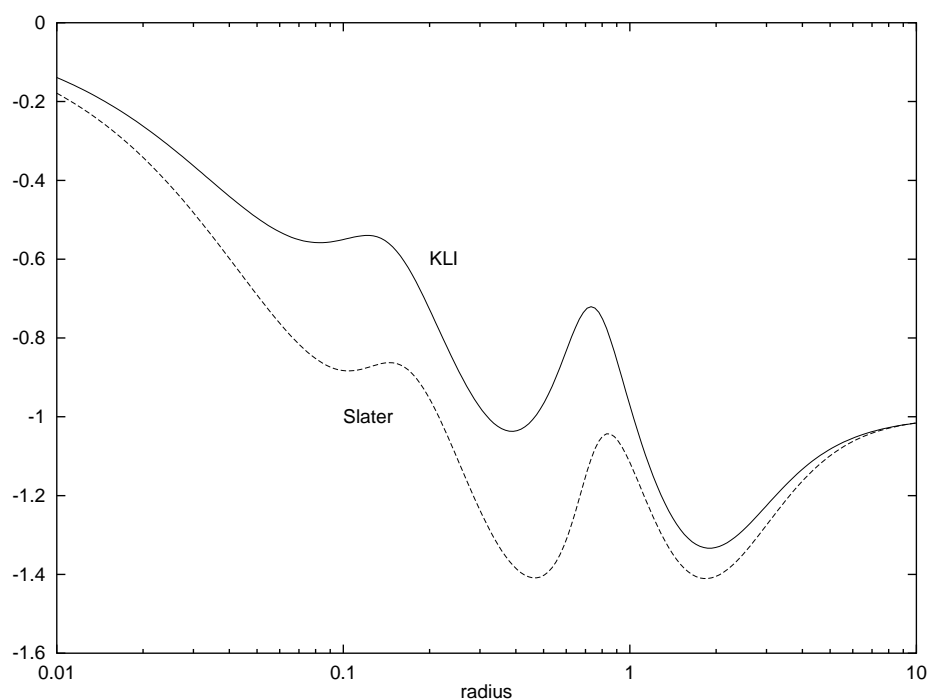


Fig. 8.20: KLI and exact Slater spin-up exchange potential functions multiplied with the radius, $rv_{x\uparrow}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\uparrow}^{\text{Slat}}(r)$ (dashed line), for Ar (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

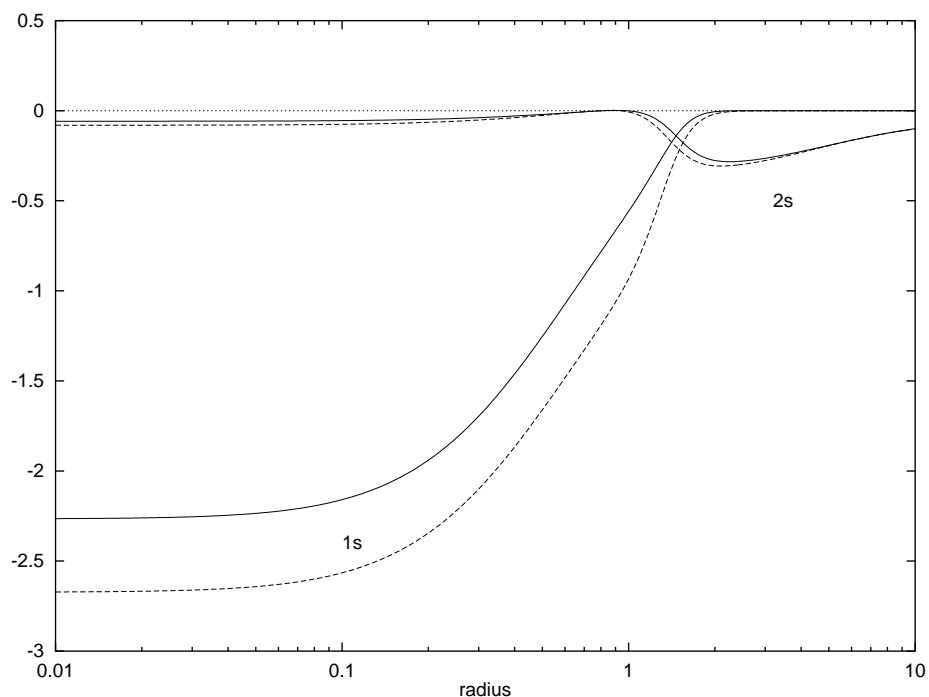


Fig. 8.21: Additive components $v_{x\uparrow i}^{\text{KLI}}(r)$ (continuous lines) and $v_{x\uparrow i}^{\text{Sla}}(r)$ (dashed lines) of the exact exchange spin-up potential functions for Li. Atomic units are used and the r -axis is scaled logarithmically.

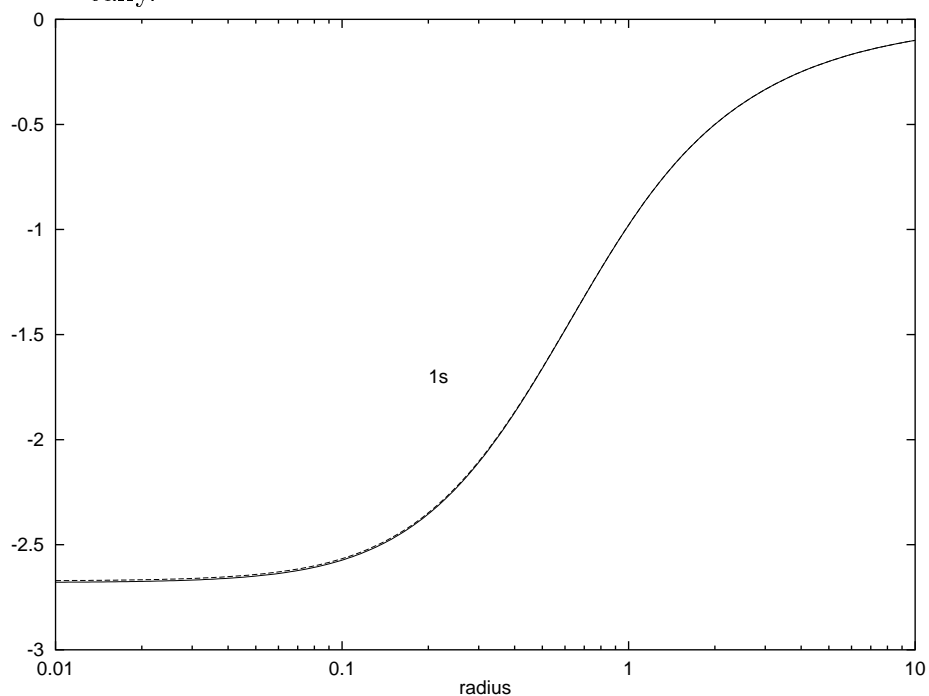


Fig. 8.22: Additive components $v_{x\downarrow i}^{\text{KLI}}(r)$ (continuous line) and $v_{x\downarrow i}^{\text{Sla}}(r)$ (dashed line) of the exact exchange spin-down potential functions for Li. Atomic units are used and the r -axis is scaled logarithmically.

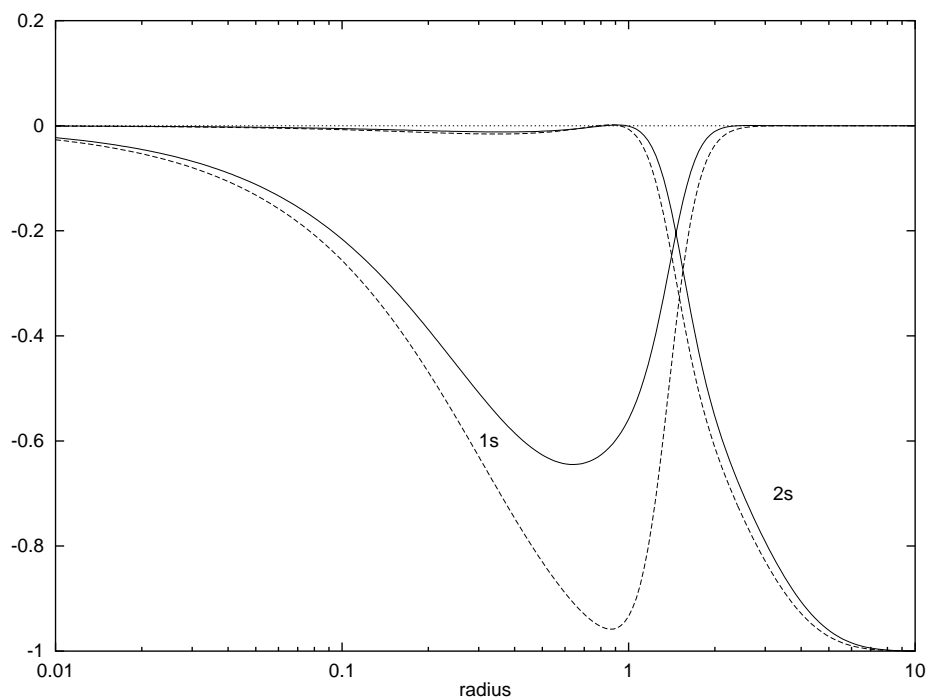


Fig. 8.23: Additive components $rv_{x\uparrow i}^{\text{KLI}}(r)$ (continuous lines) and $rv_{x\uparrow i}^{\text{Sl}_a}(r)$ (dashed lines) of the exact exchange spin-up potential functions multiplied with the radius for Li. Atomic units are used and the r -axis is scaled logarithmically.

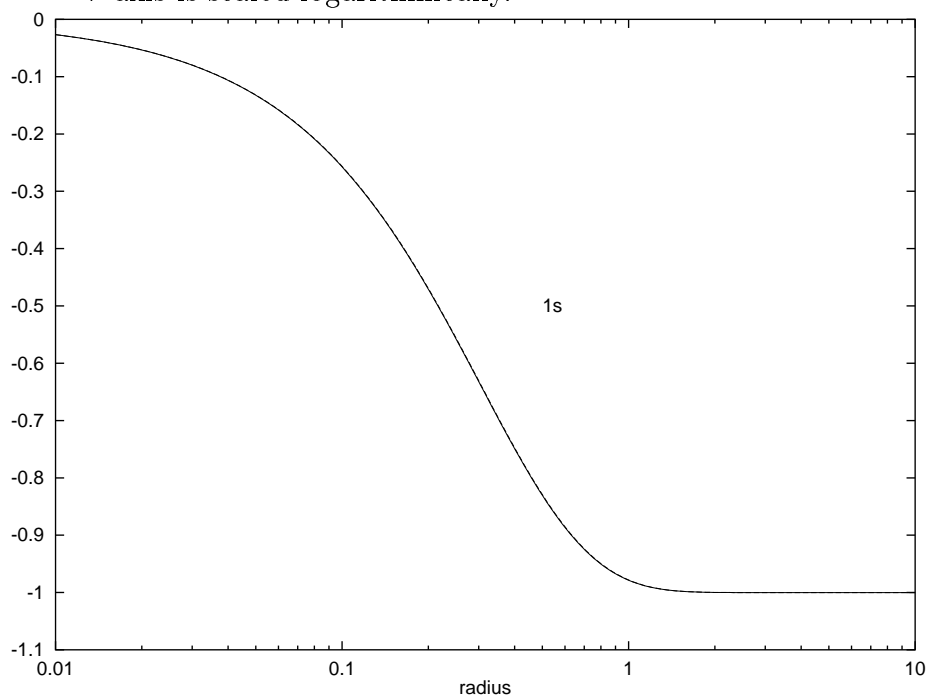


Fig. 8.24: Additive components $rv_{x\downarrow i}^{\text{KLI}}(r)$ (continuous line) and $rv_{x\downarrow i}^{\text{Sl}_a}(r)$ (dashed line) of the exact exchange spin-down potential functions multiplied with the radius for Li. Atomic units are used and the r -axis is scaled logarithmically.

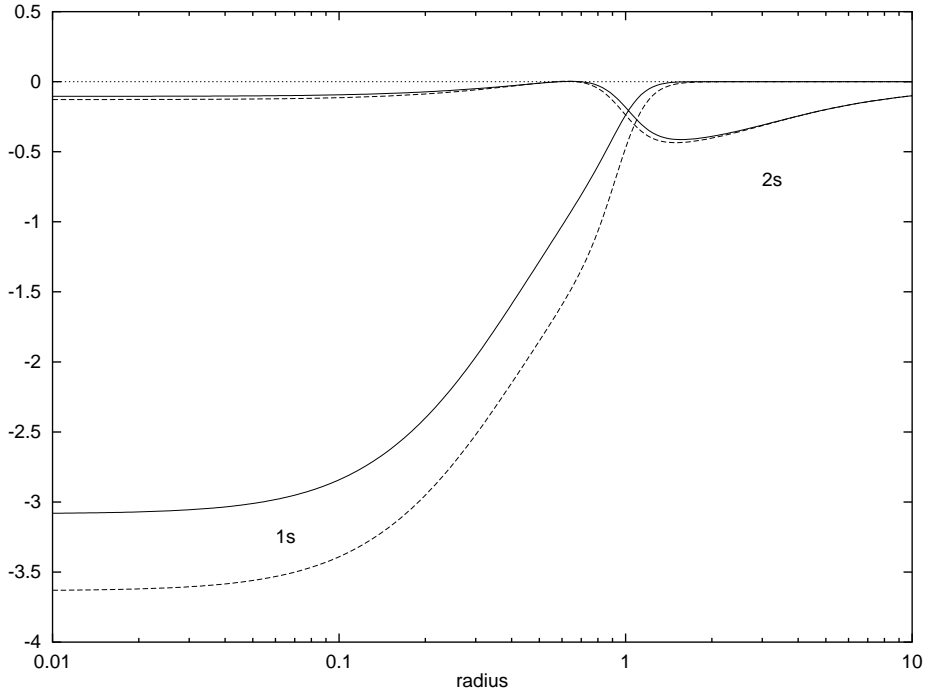


Fig. 8.25: Additive components $v_{x\uparrow i}^{\text{KLI}}(r)$ (continuous lines) and $v_{x\uparrow i}^{\text{Sl}_a}(r)$ (dashed lines) of the exact exchange spin-up potential functions for Be (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

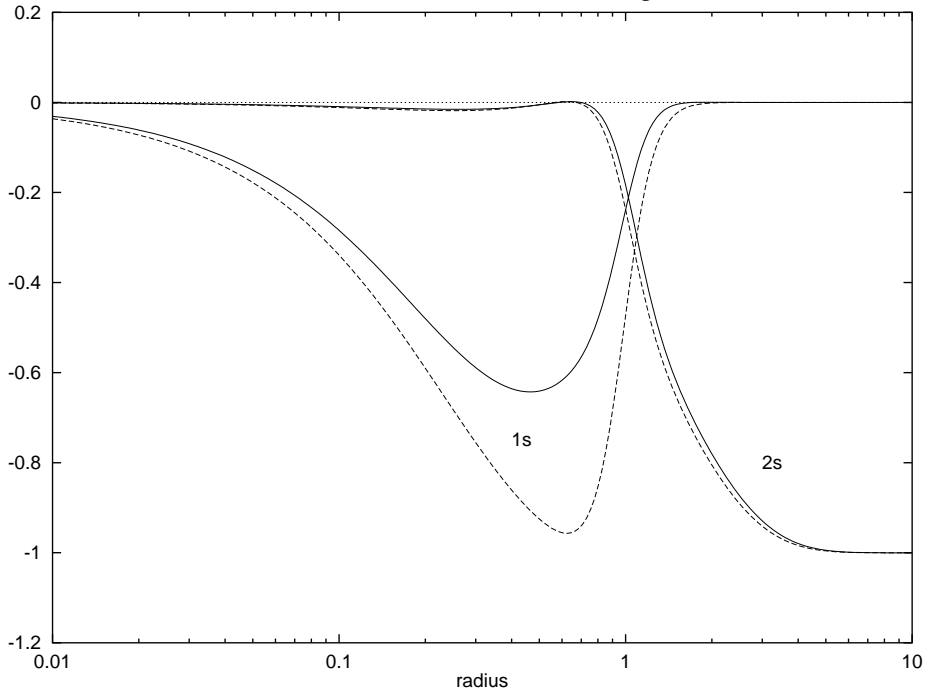


Fig. 8.26: Additive components $rv_{x\uparrow i}^{\text{KLI}}(r)$ (continuous lines) and $rv_{x\uparrow i}^{\text{Sl}_a}(r)$ (dashed lines) of the exact exchange spin-up potential functions multiplied with the radius for Be (the spin-down results produce the same figure). Atomic units are used and the r -axis is scaled logarithmically.

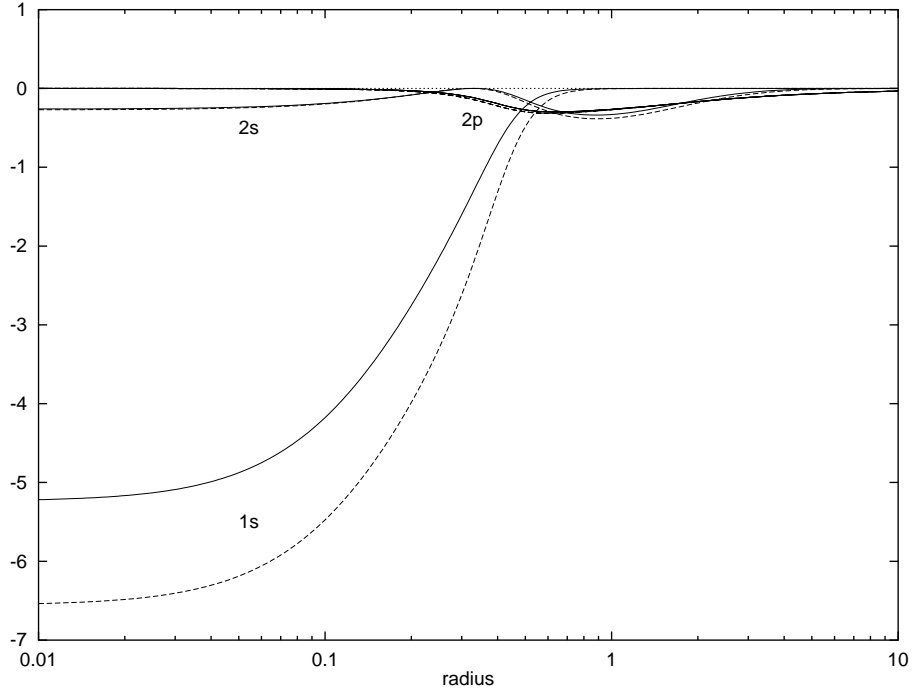


Fig. 8.27: Additive components $v_{x\uparrow i}^{KLI}(r)$ (continuous lines) and $v_{x\uparrow i}^{Sla}(r)$ (dashed lines) of the exact exchange spin-up potential functions for N. Atomic units are used and the r -axis is scaled logarithmically.

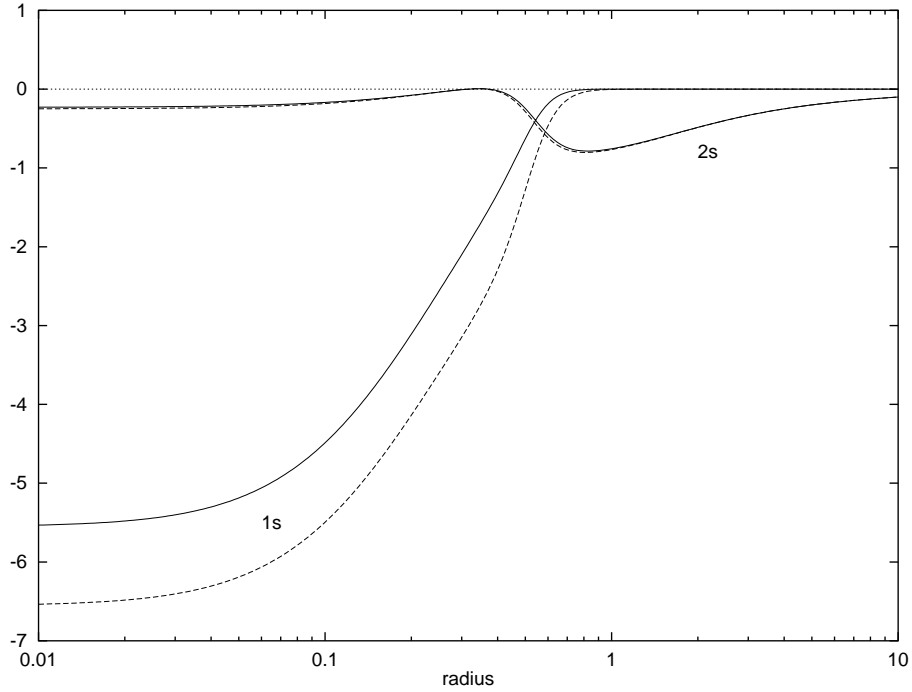


Fig. 8.28: Additive components $v_{x\downarrow i}^{KLI}(r)$ (continuous lines) and $v_{x\downarrow i}^{Sla}(r)$ (dashed lines) of the exact exchange spin-down potential functions for N. Atomic units are used and the r -axis is scaled logarithmically.

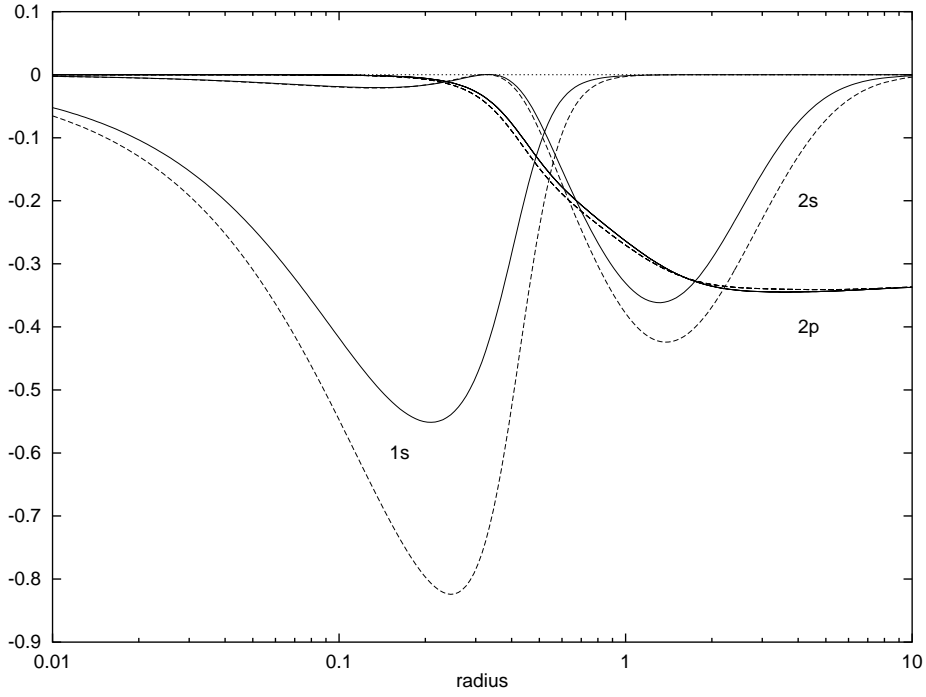


Fig. 8.29: Additive components $rv_{x\uparrow i}^{\text{KLI}}(r)$ (continuous lines) and $rv_{x\uparrow i}^{\text{SLa}}(r)$ (dashed lines) of the exact exchange spin-up potential functions multiplied with the radius for N. Atomic units are used and the r -axis is scaled logarithmically.

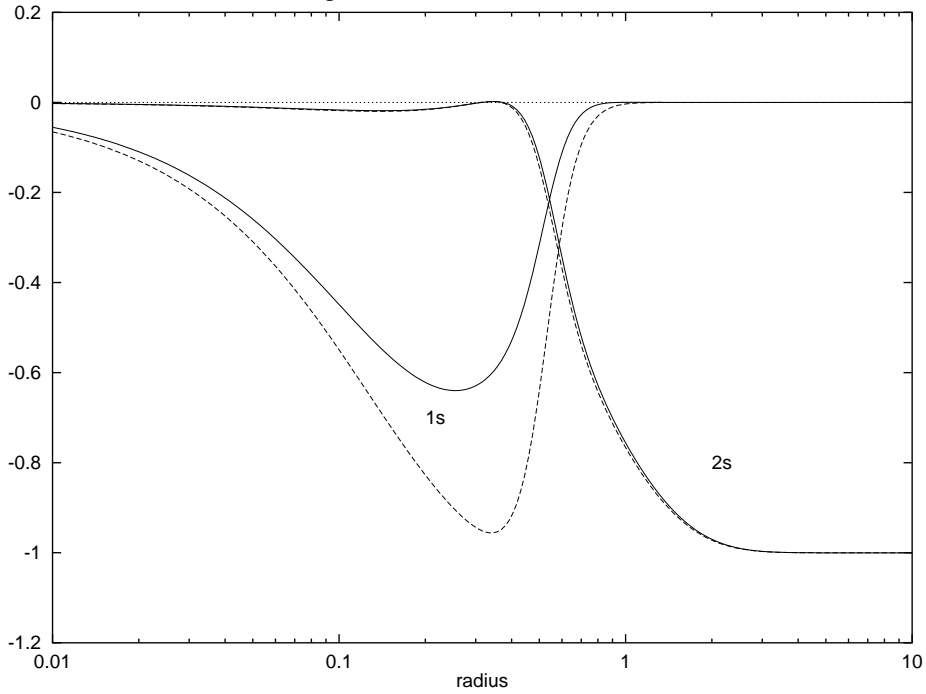


Fig. 8.30: Additive components $rv_{x\downarrow i}^{\text{KLI}}(r)$ (continuous lines) and $rv_{x\downarrow i}^{\text{SLa}}(r)$ (dashed lines) of the exact exchange spin-down potential functions multiplied with the radius for N. Atomic units are used and the r -axis is scaled logarithmically.

Finally, we have summarized in a table the total energies of our six atoms; they were obtained from spin-unrestricted Hartree-Fock (SUHF) calculations, from our KLI calculations which are in good agreement with previous calculations [111, 124], and from our exact Slater calculations.

In a further table we compare the highest occupied energy eigenvalues for each spin obtained from the same calculations for the six atoms.

For both tables, the SUHF results have been taken from Ref. [111].

Tab. 8.1: Absolute value in atomic units of the total energy of Li, Be, N, P, Cl, and Ar in spin-unrestricted Hartree-Fock (SUHF) calculations, in our KLI calculations, and in our exact Slater calculations. The SUHF results are from Ref. [111].

Atom	Configuration	SUHF	KLI	Slater
Li	$2s^1$	7.43275	7.4386	7.5606
Be	$2s^2$	14.57302	14.5943	14.9536
N	$2p^3$	54.40455	54.4374	55.8412
P	$3p^3$	340.7193	340.6123	347.9789
Cl	$3p^5$	459.4826	459.3510	468.5441
Ar	$3p^6$	526.8175	526.6661	536.8652

We notice that the KLI energies are very close to the SUHF results whereas the exact Slater results exhibit considerable deviations from both the SUHF and the KLI results.

Tab. 8.2: Absolute values in atomic units of the highest occupied energy eigenvalues of each spin projection for Li, Be, N, P, Cl, and Ar. For Be and Ar only one eigenvalue is given since the $2s$ orbitals in Be and all the $3p$ orbitals in Ar are degenerate. The results are from spin-unrestricted Hartree-Fock (SUHF) calculations, from our KLI calculations, and from our exact Slater calculations. The SUHF results are from Ref. [111].

Atom	Configuration	State	SUHF	KLI	Slater
Li	$2s^1$	$2s \uparrow$	0.1964	0.1962	0.2131
		$1s \downarrow$	2.4687	2.4675	2.4211
Be	$2s^2$	$2s$	0.3092	0.3089	0.3265
N	$2p^3$	$2p \uparrow$	0.5709	0.5713	0.6236
		$2s \downarrow$	0.7258	0.7255	0.7357
P	$3p^3$	$3p \uparrow$	0.3921	0.3907	0.4288
		$3s \downarrow$	0.5562	0.5548	0.5940
Cl	$3p^5$	$3p \uparrow$	0.5292	0.5251	0.5709
		$3p \downarrow$	0.4734	0.4907	0.5270
Ar	$3p^6$	$3p$	0.5910	0.5893	0.6383

8.2 Rare gas solids

We implemented the formulas for the KLI exchange potential and for the exact Slater exchange potential, both as given in the second approach, section 6.5.2 and section 7.3, into the ASW program and performed self-consistent calculations for solid Ne, Ar, and Kr in the face centered cubic (fcc) structure. Since in these special cases with only one atom per unit cell we have $Q_{ik\sigma}^{\mathbf{P}} = \delta_{ik}$ and $m = 1$ in the formulas Eq. (6.104) and Eq. (6.119), we did not have to implement the coefficients $D_L(\mathbf{P} - \mathbf{P}', \mathbf{0})$. We used as lattice constants 8.435 a.u. for Ne, 10.036 a.u. for Ar, and 10.670 a.u. for Kr. As basis functions we chose 3s-, 2p-, and 3d-functions for Ne, 4s-, 3p-, and 4d-functions for Ar, and 5s-, 4p-, and 4d-functions for Kr.

Our calculations show that the ASW program is by the use of KLI slowed down by a factor of about 15. However, the KLI part of the program has not yet been optimized with respect to computer time. For our SCF calculations we used a linear mixing for the potential and we do not use the momentum analysis anymore, that is, we use the electron density gained from the band structure part of the program to determine the Bessel and Hankel functions in the atomic part of the program. We noticed that the convergence is rather poor; we needed up to 100 SCF cycles.

In Figs. 8.31 and 8.32 on page 98 we compare the obtained KLI exchange potential functions $v_x(r)$ and of the functions $rv_x(r)$ for the free Ar atom and solid Ar. Figs. 8.33 and 8.34 on page 99 show the same comparison for the Slater potential. It is obvious that the functions from the ASW calculations and from the atomic calculations are similar over a wide range for radii distinctly smaller than the atomic sphere radius. The increasing deviations for larger r -values are due to the finite lattice constant in the ASW program and the resulting electronic charge overlap.

Furthermore on pages 100 and 101 we show the KLI exchange potentials and the exact Slater exchange potentials for Ar from ASW and atomic calculations for different ranges of the radial mesh. The figures 8.36 and 8.38 which are taken from the literature allow a comparison with a variety of exchange potential functions. Here we see the similarity of the optimized exchange potential (OEP) and the KLI approximations and also the difference to the traditionally used Kohn-Sham exchange.

(The text continues on page 102.)

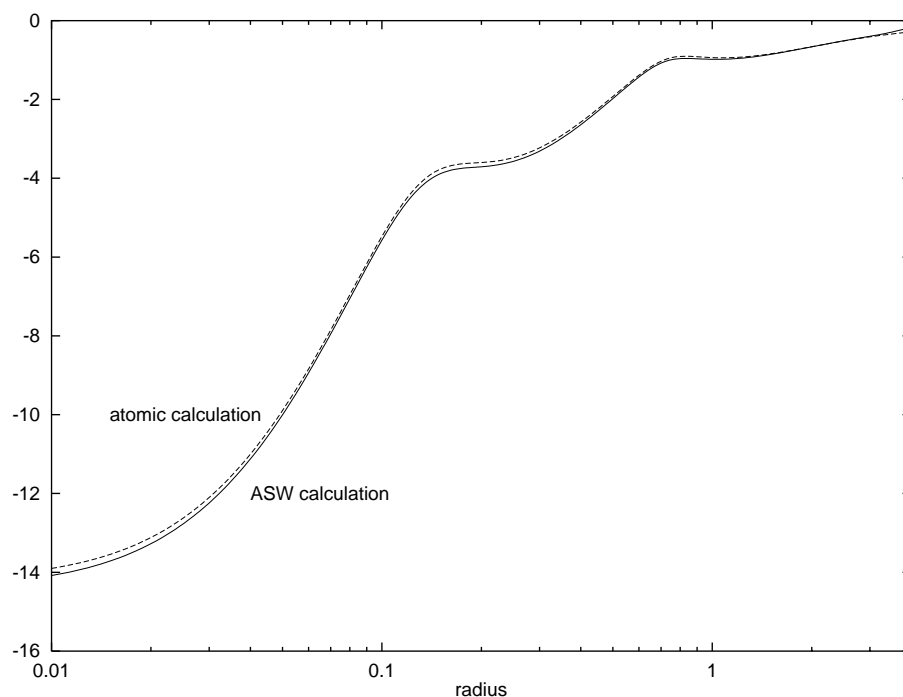


Fig. 8.31: KLI exchange potential functions $v_x^{\text{KLI}}(r)$ for Ar from the ASW program (continuous line) and from the program for atomic calculations (dashed line). Atomic units are used and the r -axis is scaled logarithmically.

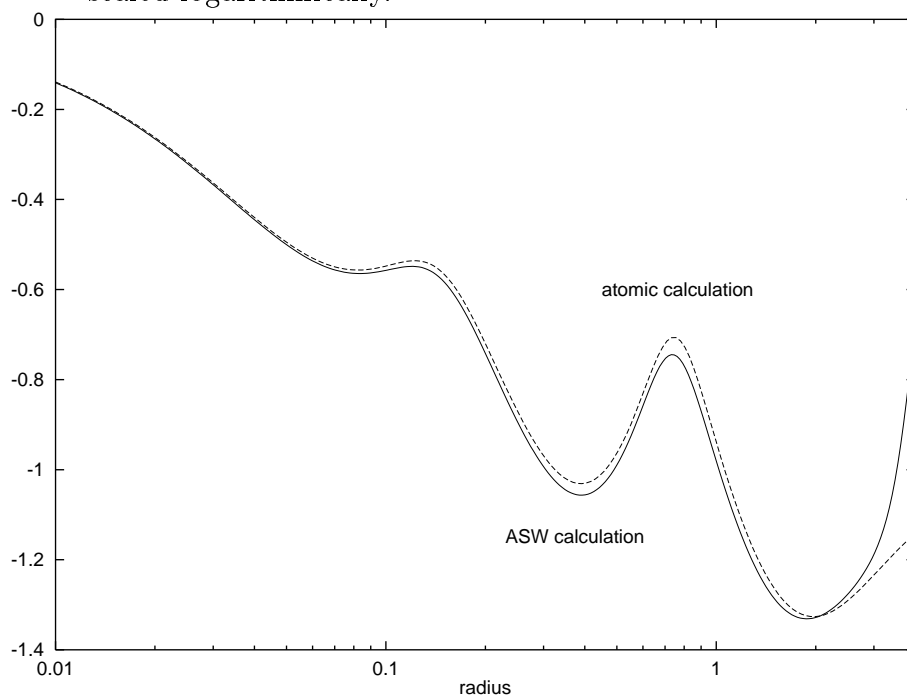


Fig. 8.32: KLI exchange potential functions multiplied with the radius, $r v_x^{\text{KLI}}(r)$, for Ar from the ASW program (continuous line) and from the program for atomic calculations (dashed line). Atomic units are used and the r -axis is scaled logarithmically.

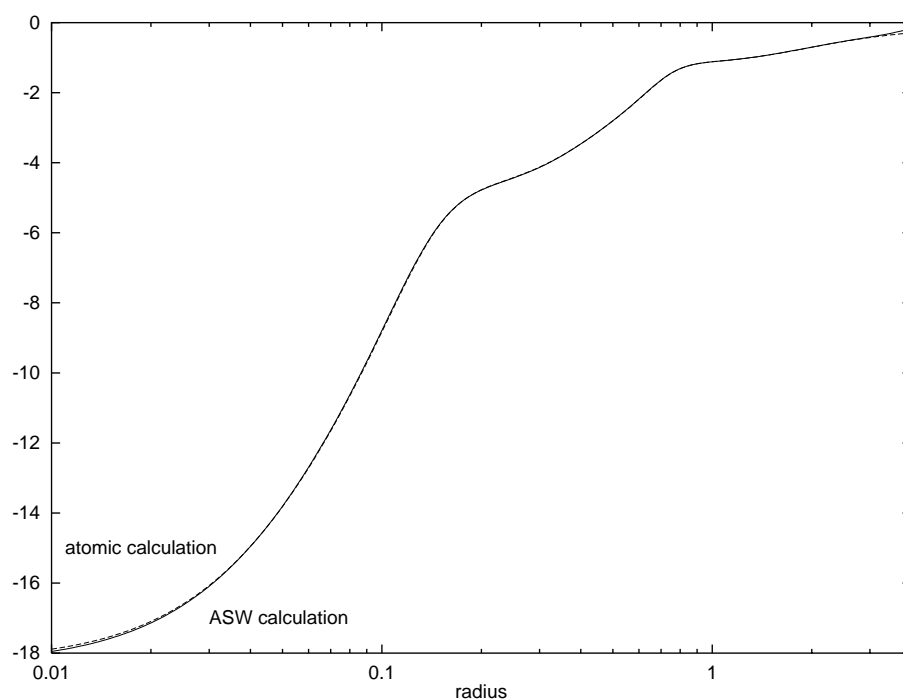


Fig. 8.33: Exact Slater exchange potential functions $v_x^{\text{Sla}}(r)$ for Ar from the ASW program (continuous line) and from the program for atomic calculations (dashed line). Atomic units are used and the r -axis is scaled logarithmically.

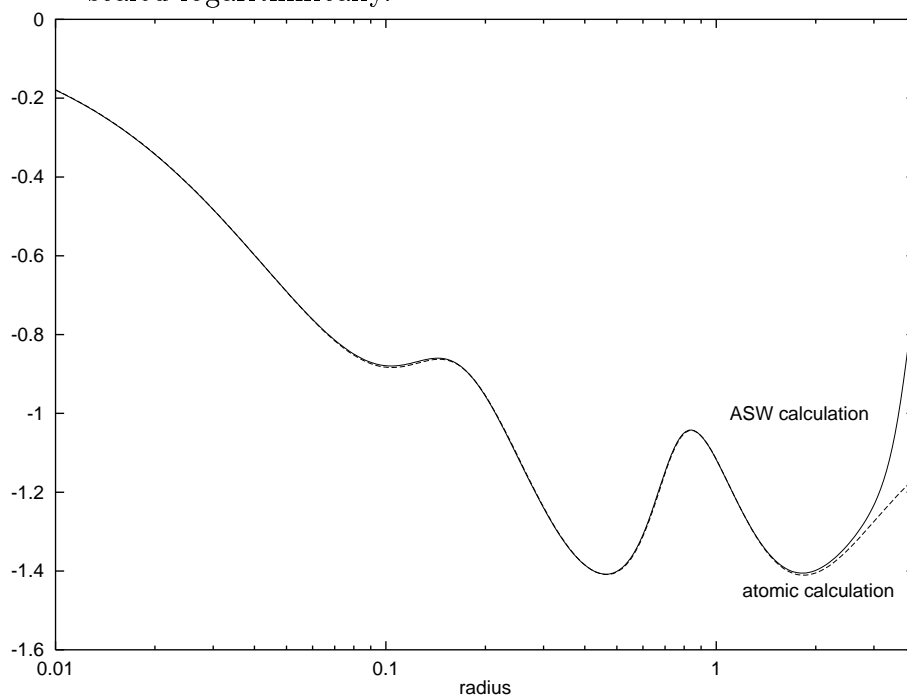


Fig. 8.34: Exact Slater exchange potential functions multiplied with the radius, $r v_x^{\text{Sla}}(r)$, for Ar from the ASW program (continuous line) and from the program for atomic calculations (dashed line). Atomic units are used and the r -axis is scaled logarithmically.

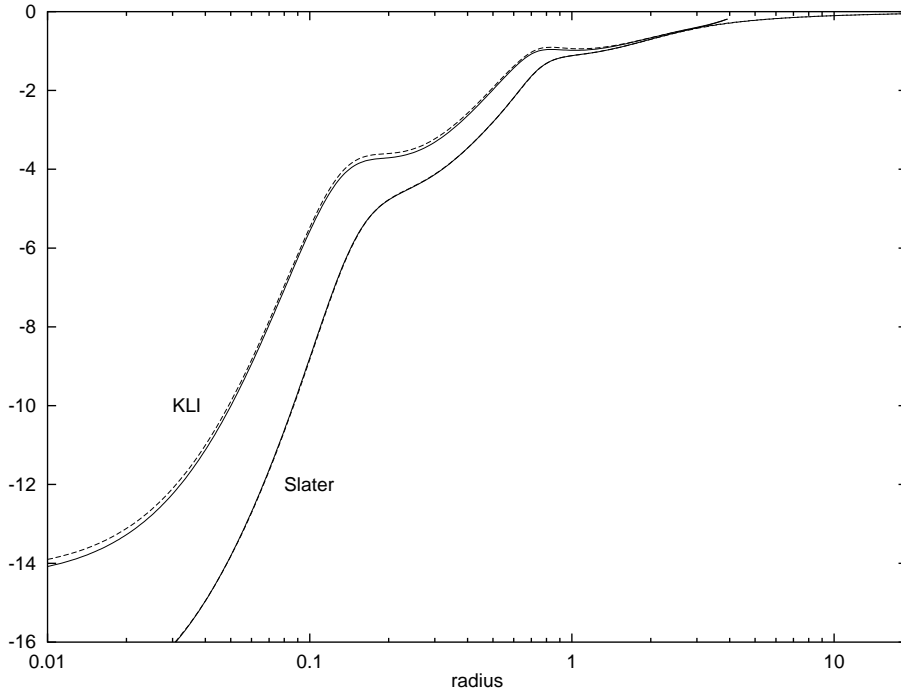


Fig. 8.35: KLI and exact Slater exchange potential functions $v_x(r)$ for Ar from the ASW program (continuous lines) and from the program for atomic calculations (dashed lines). Atomic units are used and the r -axis is scaled logarithmically.

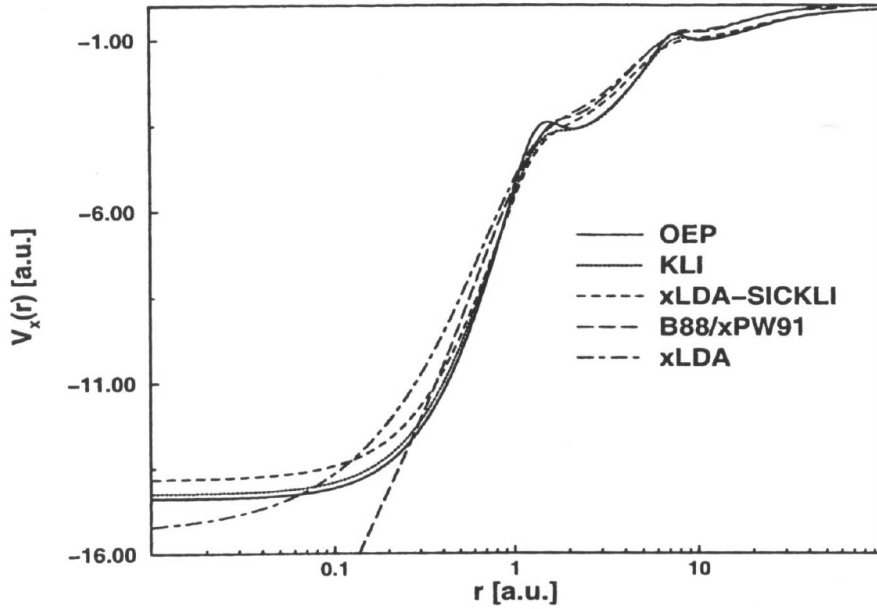


Fig. 8.36: (from Ref. [124], p. 43) Exchange potentials $v_x(r)$ for Ar from various self-consistent x-only atomic calculations. The r -axis is scaled logarithmically. xLDA is the traditional Kohn-Sham exchange-only potential; the other abbreviations are explained in Ref. [124].

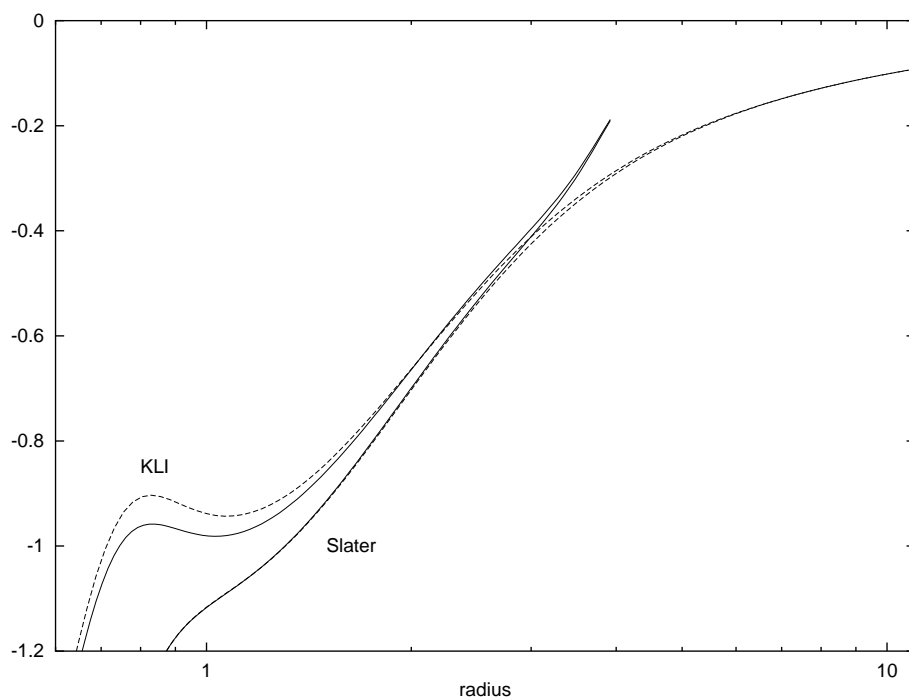


Fig. 8.37: KLI and exact Slater exchange potential functions $v_x(r)$ for Ar in the valence region. The results are from the ASW program (continuous lines) and from the program for atomic calculations (dashed lines). Atomic units are used and the r -axis is scaled logarithmically.

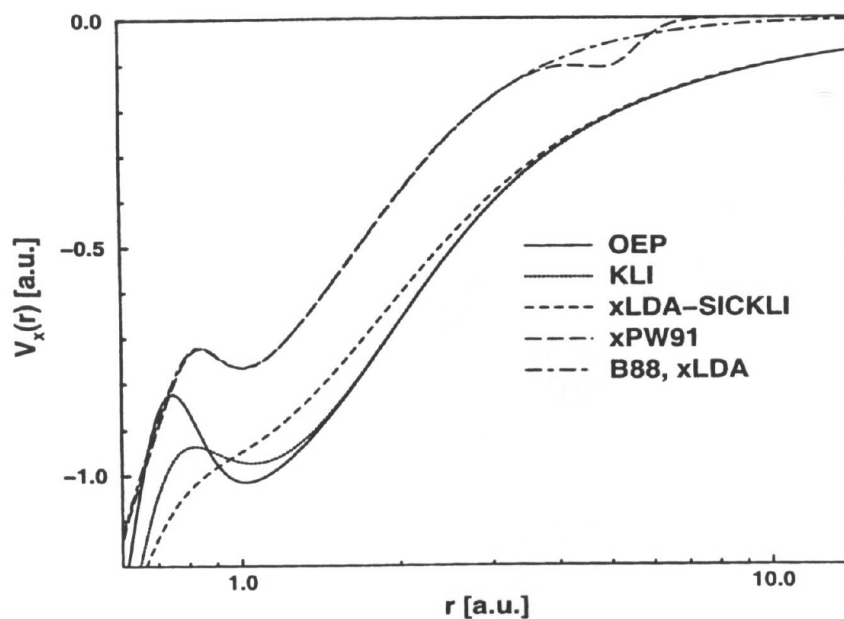


Fig. 8.38: (from Ref. [124], p. 43) Exchange potentials $v_x(r)$ for Ar from various self-consistent x-only atomic calculations in the valence region. The r -axis is scaled logarithmically.

In table 8.3 we are listing the absolute eigenvalues of Ar from atomic SUHF, KLI, and Slater calculations and from our solid state calculations. The similarity of the solid and atomic values represents the van der Waals crystals.

Tab. 8.3: Absolute eigenvalues of Ar from (left to right) the atomic SUHF and KLI calculation results presented in Table 5 of Ref. [124], from our own atomic KLI calculation (KLI a), from our solid state KLI calculation (KLI s), from our atomic Slater calculation (Slater a), and from our solid state Slater calculation (Slater s). All values are given in atomic units.

	SUHF	KLI	KLI a	KLI s	Slater a	Slater s
1s	118.6104	114.42789	114.42207	114.41190	117.06188	117.05233
2s	12.3222	11.1820	11.1800	11.1668	11.8053	11.7940
2p	9.5715	8.7911	8.7894	8.7757	9.4546	9.4429
3s	1.2774	1.0942	1.0942	1.0812	1.1508	1.1409
3p	0.5910	0.5893	0.5893	0.5579 (Γ)	0.6383	0.6131 (Γ)

Finally we show in Figs. 8.39 to 8.44 the bandstructures which we obtained from our calculations for Ne, Ar, and Kr with KLI and exact Slater. To these we add in dashed lines the bandstructures obtained from ASW calculations with LDA. The HOMO level is taken as the zero of the energy scale. Comparing the LDA and the KLI / Slater results we see that the shape of the electronic states is almost the same. There is an almost constant shift between the occupied and the unoccupied states and the width of the occupied valence bands is smaller for KLI / Slater than for the usual LDA. The HOMO-LUMO shift can be studied quantitatively from table 8.4 where we give for Ne, Ar, and Kr the experimental band gap values, the calculated KLI, Slater, and LDA band gap values, and the HF band gap values for Ne and Ar. The experimental values are from Refs. [125, 126, 6] and the HF values are from Ref. [4].

Tab. 8.4: Experimental and calculated band gap values for Ne, Ar, and Kr in eV.

	experimental	KLI	Slater	LDA	HF
Ne	21.42	15.13	16.35	11.36	25.41
Ar	14.16	9.86	10.69	8.11	18.52
Kr	11.60	8.47	8.93	6.71	

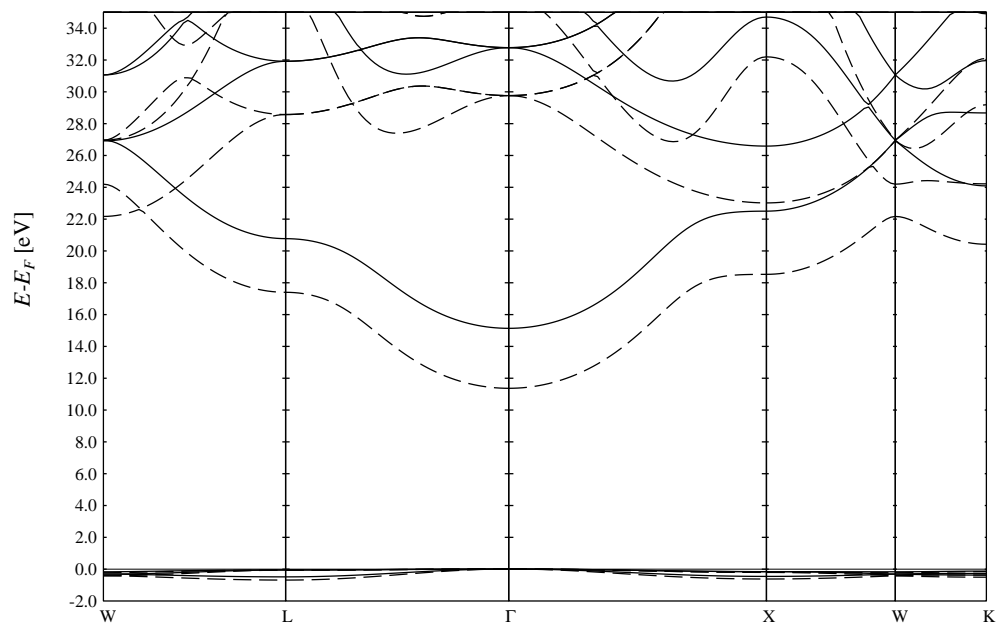


Fig. 8.39: KLI (continuous lines) and LDA (dashed lines) band structure for Ne.

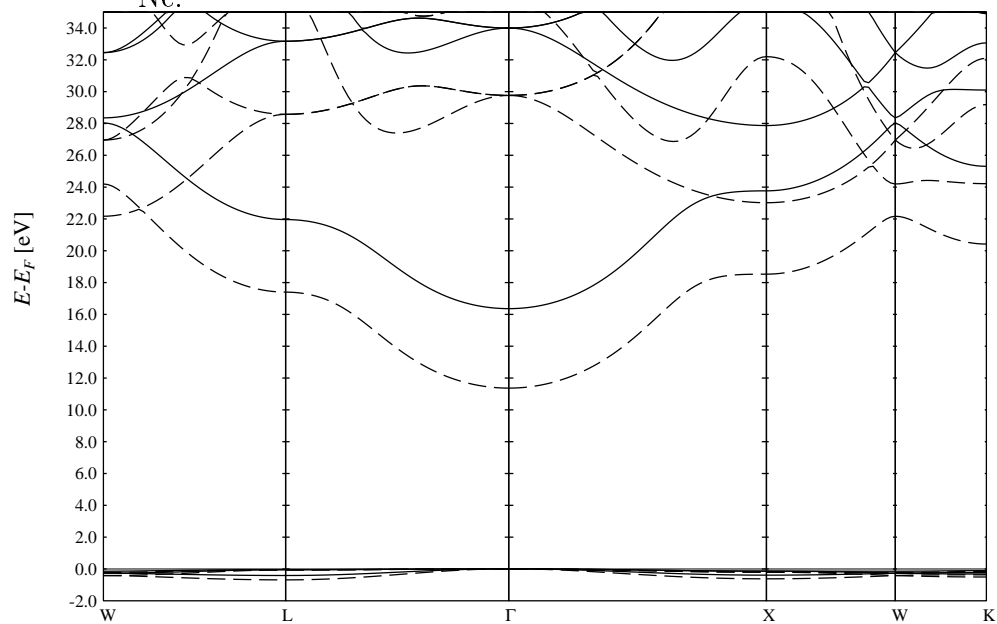


Fig. 8.40: Exact Slater (continuous lines) and LDA (dashed lines) band structure for Ne.

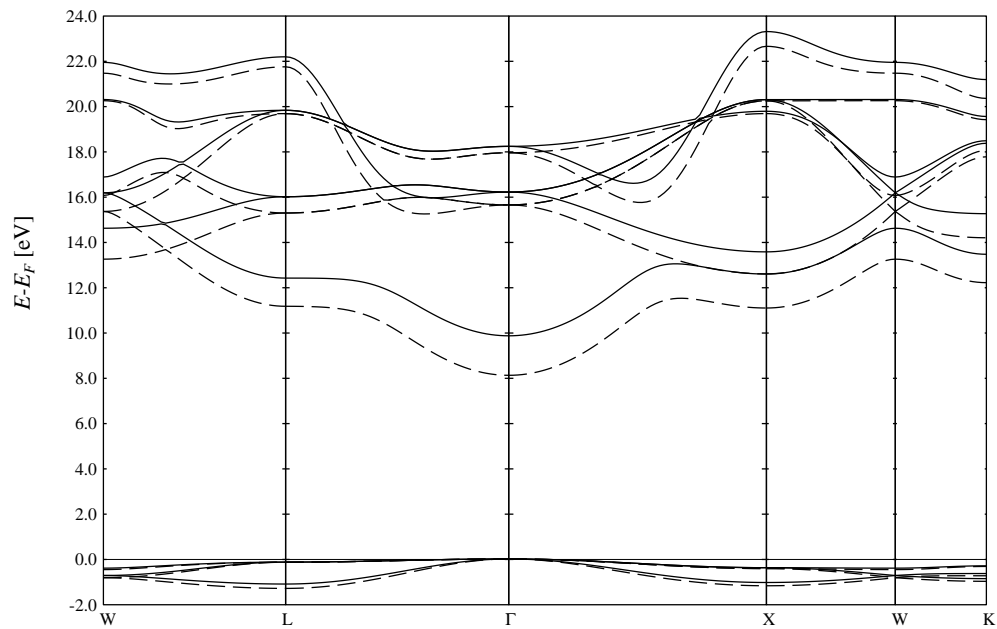


Fig. 8.41: KLI (continuous lines) and LDA (dashed lines) band structure for Ar.

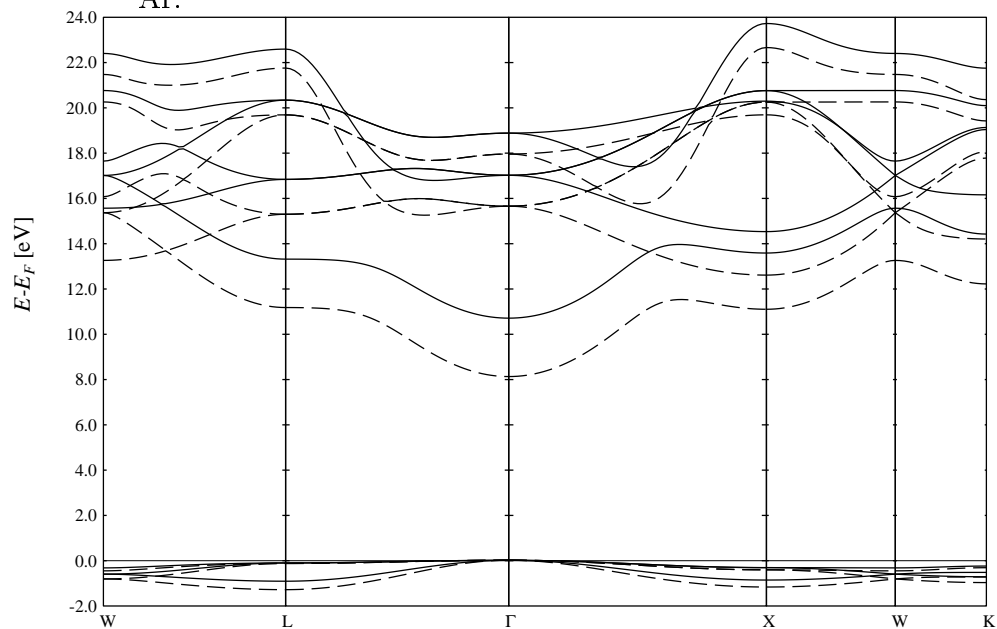


Fig. 8.42: Exact Slater (continuous lines) and LDA (dashed lines) band structure for Ar.

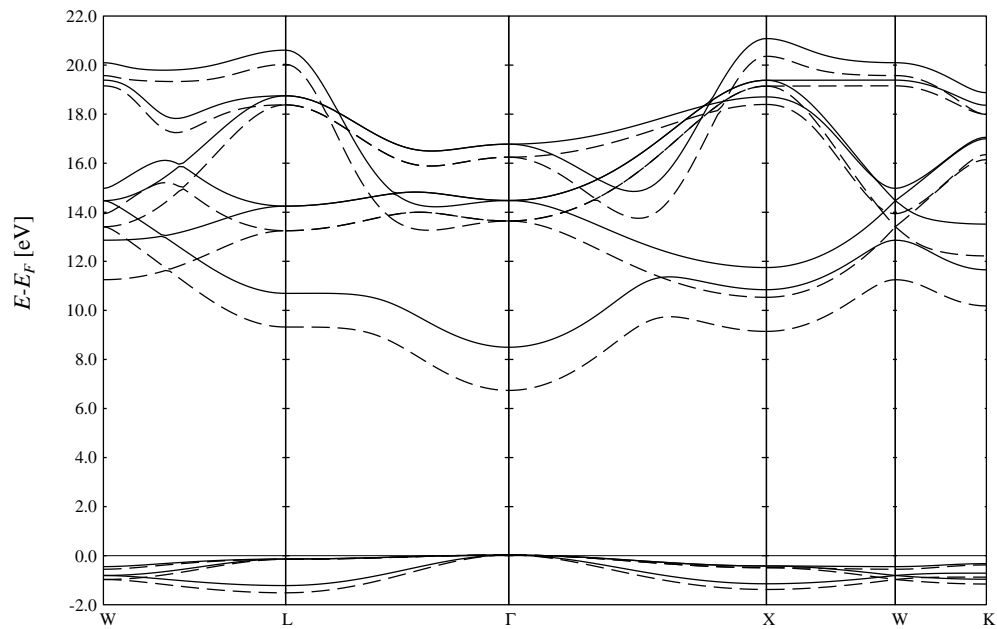


Fig. 8.43: KLI (continuous lines) and LDA (dashed lines) band structure for Kr.

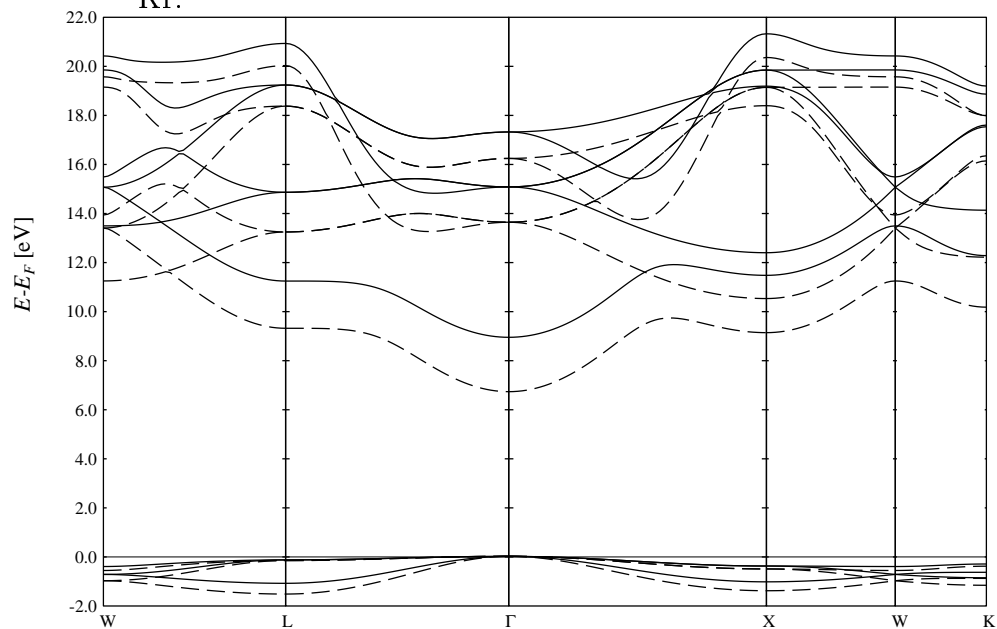


Fig. 8.44: Exact Slater (continuous lines) and LDA (dashed lines) band structure for Kr.

9. Zusammenfassung

Der Ausgangspunkt für die vorliegende Arbeit war die Frage, ob und wie man das auf dem Kohn-Sham Formalismus basierende augmented spherical waves (ASW)-Programm zur Berechnung der Elektronenstruktur so modifizieren kann, dass an Stelle des üblichen lokalen Austauschterms der Fock-Austauschterm verwendet wird.

Ziel war es, auf diese Weise ein Rechenprogramm auf Dichte-Funktional-Basis zu erhalten, bei dem die berechneten optischen Bandlücken näher am Experiment liegen als beim gewöhnlichen Dichte-Funktional-Formalismus oder beim Hartree-Fock-Verfahren.

Bekanntlich ist beim Formalismus der Dichtefunktionaltheorie (DFT) das Funktional für die Austausch-Korrelationsenergie E_{xc} der einzige Anteil am Gesamtenergiefunktional, der durch den DFT-Formalismus noch nicht festgelegt ist. Unser Augenmerk richtete sich daher auf die Frage, wie dieses Funktional der Elektronendichte $E_{xc}[n]$ bzw. das zugehörige Austausch-Korrelationspotential $v_{xc}(\mathbf{r})$, das als die funktionale Ableitung der Austausch-Korrelationsenergie nach der Elektronendichte definiert ist, geeignet zu wählen sei, wobei der zentrale Aspekt bei der Wahl des Austausch-Korrelationsenergiefunktionals darin besteht, dass es die im Coulombenergiefunktional beinhaltete Wechselwirkung der Elektronen mit sich selbst wieder aufheben muss. Dies ist gewährleistet durch Verwendung eines Nur-Austausch-Energiefunktionals E_x , das Korrelationseffekte außer Acht lässt und für E_x das sogenannte exakte Fock-Austauschenergiefunktional verwendet.

So widmeten wir uns der Frage, wie das zum exakten Fock-Austauschenergiefunktional gehörige exakte Austauschpotential, d.h. die funktionale Ableitung der exakten Austauschenergie nach der Elektronendichte, zu berechnen sei. Obwohl die exakte Austauschenergie als explizites Funktional der Kohn-Sham Orbitale bekannt ist, stellt sich heraus, dass es sich dabei um kein triviales Problem handelt und man in der praktischen Durchführung auf Näherungen angewiesen ist.

Als sehr vielversprechendes Verfahren ergibt sich die Näherung von Krieger, Li und Iafrate, bekannt unter dem Namen KLI-Näherung. Für diese Näherung gilt, dass die mit ihr erzielten Ergebnisse in guter Übereinstimmung mit denen der sogenannten Methode des optimierten effektiven Potentials (OEP) sind, die KLI-

Methode sich jedoch durch einen erheblich geringeren Rechenaufwand auszeichnet. Auch weist sie eine Vielzahl der exakten Eigenschaften der OEP-Methode auf, die als Schlüsselkriterien für die Berechnung verlässlicher Bandlücken gelten. Aus der Literatur ist auch ersichtlich, dass sowohl die OEP- als auch die KLI-Methode bei den bisher erfolgten Anwendungen in Festkörperrechenprogrammen auffallend gute Ergebnisse für Bandlücken liefern.

Aus den genannten Gründen wurden in dieser Arbeit zunächst die mathematischen Ausdrücke des KLI-Formalismus in allen Einzelheiten für Atome entwickelt und in ein Programm für Atomrechnungen implementiert.

Zusätzlich ist es uns gelungen, durch mehrmalige Anwendung der Kettenregel für funktionale Ableitungen und einiger plausibler Näherungen auf "direktem" Weg eine Formel für das exakte Austauschpotential herzuleiten.

Dabei stellte sich heraus, dass die von uns hergeleitete Formel identisch ist mit dem exakten Slater-Austauschpotential, auch wenn Slater bei dessen Herleitung im Jahr 1951 einen von unserer Vorgehensweise ganz verschiedenen Weg eingeschlagen hatte.

Wir implementierten nun auch das exakte Slater-Austauschpotential in das Atomprogramm.

Die Rechnungen mit dem Atomprogramm zeigen, dass unsere KLI-Werte mit früheren Daten in guter Übereinstimmung sind und dass die Ergebnisse für die Gesamtenergie mit dem Slater-Ansatz tiefer liegen als die mit der KLI-Näherung. Die Gesamtenergien in der KLI-Näherung liegen sehr nahe an den Werten, die man mit der spin-unrestricted Hartree-Fock-Methode erhält. Auch zeigt ein Vergleich der berechneten Energiewerte mit Ergebnissen aus Hartree-Fock Rechnungen, dass zwar die KLI-Resultate mit diesen in guter Übereinstimmung sind, die Slater-Resultate jedoch sowohl von den Hartree-Fock- als auch von den KLI-Resultaten erheblich abweichen.

Weiterhin zeigt sich, dass der prinzipielle Verlauf der Austauschpotentiale für die beiden Ansätze sehr ähnlich ist und dass insbesondere in beiden Fällen wirklich das korrekte asymptotische Verhalten der Austauschpotentiale vorliegt. Es ist jedoch offenkundig, dass die Funktionswerte der Slater-Austauschpotentiale in der Nähe der Atomkerne erhebliche Abweichungen von denen der KLI-Austauschpotentiale aufweisen.

In einem zweiten Schritt wurden die Formeln der KLI-Näherung für ein spezielles Bandstrukturprogramm, das ASW-Programm, ausgearbeitet. Das ASW-Programm wurde von Prof. Kübler entwickelt und wird an der Technischen Universität Darmstadt sowohl in der Physik als auch in der Chemie intensiv verwendet. Wir implementierten sowohl den KLI- als auch den exakten Slater-Formalismus in dieses Programm.

Mit dem Programm wurden erste Testrechnungen mit KLI- und Slater-Formalismus für die Edelgase durchgeführt und die Ergebnisse verglichen mit den Daten aus Rechnungen für freie Atome. Der Quotient in der optischen Bandlücke $\Delta E_{g,\text{theorie}}/\Delta E_{g,\text{exp}}$ erhöht sich im Schnitt von .55 für LDA auf .75 bei KLI / Slater. Dieses Ergebnis belegt, dass die Anwendung der KLI-Näherung im ASW-Programm beim Studium von Fragen, die die Größe der Bandlücke betreffen, empfehlenswert ist. Allerdings verringert sich die Dispersion der besetzten Zustände gegenüber LDA, was möglicherweise dazu führt, dass die berechnete Breite der besetzten Bänder geringer als die experimentelle ist.

Da es die Verwendung des Fock-Austausches nicht erlaubt, die für das ASW-Programm und dessen Konvergenz charakteristische Momentenanalyse beizubehalten, wurde in den Rechnungen ein lineares Mixing des Potentials verwendet. Dieses Mixing muss bei zukünftigen Rechnungen durch eine neue Form des Mixings zum Erzwingen der Konvergenz ersetzt werden. Dieser praktische Aspekt der Rechnungen wurde im Rahmen dieser Arbeit nicht behandelt.

Appendix

A. Some more explicit formulas for valence electrons in the ASW program

In the ASW program Kohn-Sham orbitals $\tilde{\varphi}_{i\sigma}(\mathbf{r})$ for valence electrons are inside the atomic sphere around some point \mathbf{P} given in the form

$$\tilde{\varphi}_{i\sigma}(\mathbf{r}) = \sum_L \left[\tilde{c}_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) + \tilde{a}_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \right] \quad (\text{A.1})$$

with complex coefficients $\tilde{c}_{Li\sigma}$ and $\tilde{a}_{Li\sigma}$ and with real valued radial Hankel functions $\tilde{h}_{\ell\sigma}$ and real valued radial Bessel functions $\tilde{j}_{\ell\sigma}$.

However, these functions $\tilde{\varphi}_{i\sigma}(\mathbf{r})$ are not yet normalized, i.e., for

$$Q = \sum_{\mathbf{P} \in UC} \int_{S_P} \tilde{\varphi}_{i\sigma}^*(\mathbf{r}) \tilde{\varphi}_{i\sigma}(\mathbf{r}) d\mathbf{r} \quad (\text{A.2})$$

we have in general

$$Q \neq 1. \quad (\text{A.3})$$

To obtain the Fock exchange potential we renormalized the Kohn-Sham orbitals. We therefore use instead of the $\tilde{\varphi}_{i\sigma}(\mathbf{r})$ the functions

$$\varphi_{i\sigma}(\mathbf{r}) := \tilde{\varphi}_{i\sigma}(\mathbf{r}) / \sqrt{Q}, \quad (\text{A.4})$$

i.e.,

$$\varphi_{i\sigma}(\mathbf{r}) = \sum_L \left[c_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) + a_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \right] \quad (\text{A.5})$$

with

$$c_{Li\sigma}(\mathbf{P}) := \tilde{c}_{Li\sigma}(\mathbf{P}) / \sqrt{Q} \quad (\text{A.6})$$

$$a_{Li\sigma}(\mathbf{P}) := \tilde{a}_{Li\sigma}(\mathbf{P}) / \sqrt{Q}. \quad (\text{A.7})$$

For this, the number Q , Eq. (A.2), is given by

$$Q = \sum_{\mathbf{P} \in UC} q_{\mathbf{P}} \quad (\text{A.8})$$

with

$$\begin{aligned}
 q_{\mathbf{P}} &= \int_{S_P} \tilde{\varphi}_{i\sigma}^*(\mathbf{r}) \tilde{\varphi}_{i\sigma}(\mathbf{r}) d\mathbf{r} \\
 &= \int_{S_P} \sum_{LL'} \left[\begin{aligned} &\tilde{c}_{Li\sigma}^*(\mathbf{P}) \tilde{c}_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+\tilde{c}_{Li\sigma}^*(\mathbf{P}) \tilde{a}_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+\tilde{a}_{Li\sigma}^*(\mathbf{P}) \tilde{c}_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+\tilde{a}_{Li\sigma}^*(\mathbf{P}) \tilde{a}_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \end{aligned} \right] Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) d\mathbf{r} \\
 &= \sum_L \int_0^{\bar{P}} (r, \mathbf{P})^2 \left[\begin{aligned} &|\tilde{c}_{Li\sigma}(\mathbf{P})|^2 |\tilde{h}_{\ell\sigma}(r, \mathbf{P})|^2 + \\ &+2\Re \left(\tilde{c}_{Li\sigma}^*(\mathbf{P}) \tilde{a}_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) + \\ &+|\tilde{a}_{Li\sigma}(\mathbf{P})|^2 |\tilde{j}_{\ell\sigma}(r, \mathbf{P})|^2 \end{aligned} \right] d(r, \mathbf{P}) \\
 &= \sum_{\ell} \left[\begin{aligned} &\int_0^{\bar{P}} (r, \mathbf{P})^2 |\tilde{h}_{\ell\sigma}(r, \mathbf{P})|^2 d(r, \mathbf{P}) \sum_{m_{\ell}} |\tilde{c}_{Li\sigma}(\mathbf{P})|^2 + \\ &+\int_0^{\bar{P}} (r, \mathbf{P})^2 \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) d(r, \mathbf{P}) 2\Re \left(\sum_{m_{\ell}} \tilde{c}_{Li\sigma}^*(\mathbf{P}) \tilde{a}_{Li\sigma}(\mathbf{P}) \right) + \\ &+\int_0^{\bar{P}} (r, \mathbf{P})^2 |\tilde{j}_{\ell\sigma}(r, \mathbf{P})|^2 d(r, \mathbf{P}) \sum_{m_{\ell}} |\tilde{a}_{Li\sigma}(\mathbf{P})|^2 \end{aligned} \right]
 \end{aligned} \tag{A.9}$$

where we used in the second step the orthonormality of the real valued spherical harmonics.

Now, using the renormalized Kohn-Sham orbitals $\varphi_{i\sigma}(\mathbf{r})$, Eq. (A.5), we can calculate the valence electron density $n_{\sigma}(\mathbf{r})$ inside some atomic sphere around \mathbf{P} ; hereby the sum over i means the sum over all occupied valence states:

$$\begin{aligned}
 n_{\sigma}(\mathbf{r}) &= \sum_i \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \\
 &= \sum_i \sum_{LL'} \left[\begin{aligned} &c_{Li\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+c_{Li\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+a_{Li\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+a_{Li\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \end{aligned} \right] Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \\
 &= \sum_i \sum_{LL'L''} \left[\begin{aligned} &c_{Li\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+c_{Li\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+a_{Li\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ &+a_{Li\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \end{aligned} \right] C_{LL'L''} Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}).
 \end{aligned} \tag{A.10}$$

The spherically symmetric part $n_{\sigma}(r, \mathbf{P})$ of $n_{\sigma}(\mathbf{r})$ is then obviously given by the $L'' = (0, 0)$ contribution which due to

$$Y_{(0,0)}(\hat{\mathbf{r}}) = \frac{1}{\sqrt{4\pi}} \tag{A.11}$$

and

$$C_{LL'(0,0)} = \frac{1}{\sqrt{4\pi}} \int Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \frac{1}{\sqrt{4\pi}} \delta_{LL'} \tag{A.12}$$

implies

$$\begin{aligned}
 n_\sigma(r, \mathbf{P}) &= \frac{1}{4\pi} \sum_i \sum_L \left[\begin{aligned} &|c_{Li\sigma}(\mathbf{P})|^2 \left| \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \right|^2 + \\ &+ 2\Re(c_{Li\sigma}^*(\mathbf{P}) a_{Li\sigma}(\mathbf{P})) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) + \\ &+ |a_{Li\sigma}(\mathbf{P})|^2 \left| \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right|^2 \end{aligned} \right] \quad (\text{A.13}) \\
 &= \frac{1}{4\pi} \sum_\ell \left[\bar{c}_{\ell\sigma}(\mathbf{P}) \left| \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \right|^2 + \bar{b}_{\ell\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) + \bar{a}_{\ell\sigma}(\mathbf{P}) \left| \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right|^2 \right]
 \end{aligned}$$

where we have defined new constants

$$\bar{c}_{\ell\sigma}(\mathbf{P}) := \sum_{m_\ell} \sum_i |c_{Li\sigma}(\mathbf{P})|^2, \quad (\text{A.14})$$

$$\bar{b}_{\ell\sigma}(\mathbf{P}) := \sum_{m_\ell} \sum_i 2\Re(c_{Li\sigma}^*(\mathbf{P}) a_{Li\sigma}(\mathbf{P})), \quad (\text{A.15})$$

$$\bar{a}_{\ell\sigma}(\mathbf{P}) := \sum_{m_\ell} \sum_i |a_{Li\sigma}(\mathbf{P})|^2. \quad (\text{A.16})$$

B. Detailed KLI formulas for the ASW program

In the ASW program, the Kohn-Sham orbitals for core electrons are of the form

$$\varphi_{i\sigma}(\mathbf{r}) = R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \quad (\text{here } i = (n, \ell, m_\ell)) \quad (\text{B.1})$$

for \mathbf{r} inside the atomic sphere around \mathbf{P} , and we have already seen in Appendix A that the radial parts of the Kohn-Sham orbitals for valence electrons are of the form

$$R_{i\sigma L}(r, \mathbf{P}) = c_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \quad (\text{B.2})$$

(cf. Eqs. (6.74) and (A.5)).

We want to use these concrete Kohn-Sham orbitals to rewrite the KLI formulas presented in the second approach for ASW, subsection 6.5.2.

In the following, let the indices $1\sigma, \dots, K_\sigma\sigma$ correspond to the core electrons with spin σ and let the indices $(K_\sigma + 1)\sigma, \dots, N_\sigma\sigma$ correspond to the valence electrons with spin σ .

B.1 Calculation of the functions $|\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r})$

First, the contribution from the atomic sphere S_P , Eq. (6.117), can be rewritten:

$$\begin{aligned} -\varphi_{i\sigma}(\mathbf{r}) \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' &= \sum_{k=1}^{K_\sigma} \left(-\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) + \\ &+ \sum_{k=K_\sigma+1}^{N_\sigma} \left(-\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right). \end{aligned}$$

For the calculation of the inside the atomic spheres spherically averaged functions $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ it is consequently sufficient to know the explicit formulas for the calculation of the spherical average of the functions

$$-\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (\text{B.3})$$

We present these in the following.

It is convenient, however, to introduce first the abbreviation

$$Coul_{\ell''}(f_1, f_2, (r, \mathbf{P})) := \left\{ \frac{1}{(r, \mathbf{P})^{\ell''+1}} \int_0^{(r, \mathbf{P})} (r', \mathbf{P})^{\ell''+2} f_1^*(r', \mathbf{P}) f_2(r', \mathbf{P}) d(r', \mathbf{P}) + \right. \\ \left. + (r, \mathbf{P})^{\ell''} \int_{(r, \mathbf{P})}^{\bar{P}} (r', \mathbf{P})^{1-\ell''} f_1^*(r', \mathbf{P}) f_2(r', \mathbf{P}) d(r', \mathbf{P}) \right\}.$$

Case 1: Both $i\sigma$ and $k\sigma$ correspond to core states:

$$\begin{aligned} \varphi_{i\sigma}(\mathbf{r}) &= R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\ \varphi_{k\sigma}(\mathbf{r}) &= R_{n'\ell'\sigma}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \end{aligned}$$

for \mathbf{r} inside the atomic sphere S_P around \mathbf{P} .

Using the relationship

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) \quad (\text{B.4})$$

(cf. Eq. (6.58)) where $\tilde{r}_{<} (\tilde{r}_{>})$ denotes the smaller (greater) of (r, \mathbf{P}) and (r', \mathbf{P}) and the real valued Gaunt integrals $C_{LL'L''}$, Eq. (6.59), we obtain for \mathbf{r} inside S_P

$$\begin{aligned} & -\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= -R_{n\ell\sigma}(r, \mathbf{P}) R_{n'\ell'\sigma}^*(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \times \\ & \quad \int_{S_P} R_{n\ell\sigma}^*(r', \mathbf{P}) R_{n'\ell'\sigma}(r', \mathbf{P}) Y_L(\hat{\mathbf{r}}', \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}', \mathbf{P}) \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) d\mathbf{r}' \\ &= -R_{n\ell\sigma}(r, \mathbf{P}) R_{n'\ell'\sigma}^*(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \times \\ & \quad \times \sum_{L''} C_{LL'L''} \frac{4\pi}{2\ell'' + 1} \int_0^{\bar{P}} (r', \mathbf{P})^2 \frac{\tilde{r}_{<}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} R_{n\ell\sigma}^*(r', \mathbf{P}) R_{n'\ell'\sigma}(r', \mathbf{P}) d(r', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}). \end{aligned}$$

The spherical average of (B.3) inside S_P is then given by

$$-\sum_{L''} (C_{LL'L''})^2 \frac{1}{2\ell'' + 1} R_{n\ell\sigma}(r, \mathbf{P}) R_{n'\ell'\sigma}^*(r, \mathbf{P}) Coul_{\ell''}(R_{n\ell\sigma}, R_{n'\ell'\sigma}, (r, \mathbf{P})). \quad (\text{B.5})$$

Case 2: One of the indices $i\sigma$ and $k\sigma$ corresponds to a core state, the other to a valence state:

Without loss of generality we assume

$$\begin{aligned} \varphi_{i\sigma}(\mathbf{r}) &= R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\ \varphi_{k\sigma}(\mathbf{r}) &= \sum_{L'} \left(c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \end{aligned}$$

for \mathbf{r} inside S_P .

Proceeding as before we obtain

$$\begin{aligned}
& -\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \int_{S_P} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
& = -R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \sum_{L'} \left(c_{L'k\sigma}^*(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'k\sigma}^*(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \times \\
& \quad \times \int_{S_P} R_{n\ell\sigma}^*(r', \mathbf{P}) Y_L(\hat{\mathbf{r}}', \mathbf{P}) \sum_{L'''} \left(c_{L'''k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r', \mathbf{P}) + a_{L'''k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r', \mathbf{P}) \right) Y_{L'''}(\hat{\mathbf{r}}', \mathbf{P}) \\
& \quad \times \sum_{L''} \frac{4\pi}{2\ell'' + 1} \frac{\tilde{r}_{\leq}^{\ell''}}{\tilde{r}_{>}^{\ell''+1}} Y_{L''}(\hat{\mathbf{r}}', \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) d\mathbf{r}' \\
& = - \sum_{L'L''L'''} C_{LL'L''} Y_L(\hat{\mathbf{r}}, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) R_{n\ell\sigma}(r, \mathbf{P}) \times \\
& \quad \times \left(c_{L'k\sigma}^*(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'k\sigma}^*(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) \frac{4\pi}{2\ell'' + 1} \times \\
& \quad \times \left[c_{L'''k\sigma}(\mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{h}_{\ell''' \sigma}, (r, \mathbf{P})) + \right. \\
& \quad \left. + a_{L'''k\sigma}(\mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{j}_{\ell''' \sigma}, (r, \mathbf{P})) \right].
\end{aligned}$$

The spherical average of (B.3) inside S_P is then given by

$$\begin{aligned}
& - \sum_{L'L''} C_{LL'L''} \frac{1}{2\ell'' + 1} \sum_{L'''} C_{LL'L'''} R_{n\ell\sigma}(r, \mathbf{P}) \times \\
& \quad \times \left[\begin{aligned} & c_{L'k\sigma}^*(\mathbf{P}) c_{L'''k\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{h}_{\ell''' \sigma}, (r, \mathbf{P})) + \\ & + a_{L'k\sigma}^*(\mathbf{P}) c_{L'''k\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{h}_{\ell''' \sigma}, (r, \mathbf{P})) + \\ & + c_{L'k\sigma}^*(\mathbf{P}) a_{L'''k\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{j}_{\ell''' \sigma}, (r, \mathbf{P})) + \\ & + a_{L'k\sigma}^*(\mathbf{P}) a_{L'''k\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(R_{n\ell\sigma}, \tilde{j}_{\ell''' \sigma}, (r, \mathbf{P})) \end{aligned} \right]. \quad (\text{B.6})
\end{aligned}$$

Case 3: Both $i\sigma$ and $k\sigma$ correspond to valence states:

$$\begin{aligned}
\varphi_{i\sigma}(\mathbf{r}) & = \sum_L \left(c_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\
\varphi_{k\sigma}(\mathbf{r}) & = \sum_L \left(c_{Lk\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Lk\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) Y_L(\hat{\mathbf{r}}, \mathbf{P})
\end{aligned}$$

for \mathbf{r} inside S_P .

This time we start from Eq. (6.119); simply leaving the last line and the sum over k away and replacing the functions $R_{i\sigma L}$ and $R_{k\sigma L'}$ by $c_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma} + a_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}$ and $c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma} + a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}$, respectively, we straightforwardly obtain the spherical average of (B.3) inside S_P to be

$$\begin{aligned}
& - \sum_{LL'L''} C_{LL'L''} \frac{1}{2\ell''+1} \sum_{L'''L'V} C_{L''L'''L'V} \times \\
& \left[\begin{aligned}
& c_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) c_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{h}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) c_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{h}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) c_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{h}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + c_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{h}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P})) + \\
& + a_{L'''i\sigma}(\mathbf{P}) a_{Li\sigma}^*(\mathbf{P}) a_{L'IVk\sigma}^*(\mathbf{P}) a_{L'k\sigma}(\mathbf{P}) \tilde{j}_{\ell''' \sigma}(r, \mathbf{P}) \tilde{j}_{\ell'V \sigma}(r, \mathbf{P}) \text{Coul}_{\ell''}(\tilde{j}_{\ell\sigma}, \tilde{j}_{\ell'\sigma}, (r, \mathbf{P}))
\end{aligned} \right]
\end{aligned} \tag{B.7}$$

Now we consider the contributions from the remaining atomic spheres,

$$\begin{aligned}
& - \frac{1}{\sqrt{4\pi}} \sum_{k=1}^{N_\sigma} \sum_{L'} R_{i\sigma L'}(r, \mathbf{P}) R_{k\sigma L'}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ik\sigma}^{\mathbf{P}'} - \frac{1}{m} \delta_{ik} \right) \Bigg|_{\ell''=0, \kappa \rightarrow 0} \\
& \tag{B.8}
\end{aligned}$$

(cf. Eq. (6.119).

Whenever $i\sigma$ or $k\sigma$ correspond to a core state we have, say,

$$\begin{aligned}
R_{i\sigma L'}(r, \mathbf{P}) &= R_{n\ell\sigma}(r, \mathbf{P}) \delta_{LL'} \text{ and} \\
R_{k\sigma L'}(r, \mathbf{P}) &= R_{n''\ell''\sigma}(r, \mathbf{P}) \delta_{L'L''}, \text{ respectively.}
\end{aligned}$$

Consequently, for $i\sigma$ corresponding to a core state, Eq. (B.8) becomes

$$\begin{aligned}
& - \frac{1}{\sqrt{4\pi}} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ii\sigma}^{\mathbf{P}'} - \frac{1}{m} \right) \Bigg|_{\ell''=0, \kappa \rightarrow 0} - \\
& - \frac{1}{\sqrt{4\pi}} \sum_{k=K_\sigma+1}^{N_\sigma} R_{n\ell\sigma}(r, \mathbf{P}) R_{k\sigma L}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) Q_{ik\sigma}^{\mathbf{P}'} \Bigg|_{\ell''=0, \kappa \rightarrow 0} \tag{B.9}
\end{aligned}$$

and for $i\sigma$ corresponding to a valence state Eq. (B.8) becomes

$$\begin{aligned}
& - \frac{1}{\sqrt{4\pi}} \sum_{k=1}^{K_\sigma} R_{i\sigma L'''}(r, \mathbf{P}) R_{n'''\ell'''\sigma}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) Q_{ik\sigma}^{\mathbf{P}'} \Bigg|_{\ell''=0, \kappa \rightarrow 0} - \\
& - \frac{1}{\sqrt{4\pi}} \sum_{k=K_\sigma+1}^{N_\sigma} \sum_{L'} R_{i\sigma L'}(r, \mathbf{P}) R_{k\sigma L'}^*(r, \mathbf{P}) \sum_{\mathbf{P}' \in UC(\mathbf{P})} D_{L''}(\mathbf{P} - \mathbf{P}', \mathbf{0}) \left(Q_{ik\sigma}^{\mathbf{P}'} - \frac{1}{m} \delta_{ik} \right) \Bigg|_{\ell''=0, \kappa \rightarrow 0} \quad (\text{B.10})
\end{aligned}$$

Hereby the required values $Q_{ik\sigma}^{\mathbf{P}'}$ are given by (cf. Eq. (6.89))

$$Q_{ii\sigma}^{\mathbf{P}'} = \int_0^{\bar{P}'} (r', \mathbf{P}')^2 |R_{n\ell\sigma}(r', \mathbf{P}')|^2 d(r', \mathbf{P}') \quad (\text{B.11})$$

when $i\sigma$ corresponds to a core state, by

$$Q_{ik\sigma}^{\mathbf{P}'} = \int_0^{\bar{P}'} (r', \mathbf{P}')^2 \sum_{L'} R_{i\sigma L'}^*(r', \mathbf{P}') R_{k\sigma L'}(r', \mathbf{P}') d(r', \mathbf{P}') \quad (\text{B.12})$$

when both $i\sigma$ and $k\sigma$ correspond to a valence state, and by

$$Q_{ik\sigma}^{\mathbf{P}'} = \int_0^{\bar{P}'} (r', \mathbf{P}')^2 R_{n\ell\sigma}^*(r', \mathbf{P}') R_{k\sigma L}(r', \mathbf{P}') d(r', \mathbf{P}') \quad (\text{B.13})$$

when without loss of generality $i\sigma$ corresponds to a core state and $k\sigma$ corresponds to a valence state.

B.2 Calculation of the numbers $M_{ji\sigma}$

To present explicit formulas for the calculation of

$$M_{ji\sigma} = \int \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} d\mathbf{r}, \quad (\text{B.14})$$

Eq. (6.77), we again distinguish three cases.

Case 1: Both $i\sigma$ and $j\sigma$ correspond to core states:

$$\begin{aligned}
\varphi_{i\sigma}(\mathbf{r}) &= R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\
\varphi_{j\sigma}(\mathbf{r}) &= R_{n'\ell'\sigma}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P})
\end{aligned}$$

for \mathbf{r} inside S_P .

Assuming $n_\sigma(\mathbf{r})$ to be spherically symmetric inside each atomic sphere and using Eqs. (6.61), (6.62), and (6.59) we obtain

$$\begin{aligned}
M_{ji\sigma} &= \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 |R_{n'\ell'\sigma}(r, \mathbf{P})|^2 (Y_L(\hat{\mathbf{r}}, \mathbf{P}))^2 (Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}))^2 d\mathbf{r} \\
&= \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 |R_{n'\ell'\sigma}(r, \mathbf{P})|^2 \sum_{L''} C_{LLL''} Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) (Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}))^2 d\mathbf{r} \\
&= \left(\sum_{L''} C_{LLL''} C_{L'L'L''} \right) \sum_{\mathbf{P}} \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 |R_{n'\ell'\sigma}(r, \mathbf{P})|^2 d(r, \mathbf{P}) \quad (\text{B.15})
\end{aligned}$$

Case 2: One of the indices $i\sigma$ and $j\sigma$ corresponds to a core state, the other to a valence state:

Without loss of generality we assume

$$\begin{aligned}
\varphi_{i\sigma}(\mathbf{r}) &= R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\
\varphi_{j\sigma}(\mathbf{r}) &= \sum_{L'} \left(c_{L'j\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'j\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P})
\end{aligned}$$

for \mathbf{r} inside S_P .

Proceeding as before we obtain

$$\begin{aligned}
M_{ji\sigma} &= \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} \sum_{L'} \left(c_{L'j\sigma}^*(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'j\sigma}^*(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \times \\
&\quad \times \sum_{L''} \left(c_{L''j\sigma}(\mathbf{P}) \tilde{h}_{\ell''\sigma}(r, \mathbf{P}) + a_{L''j\sigma}(\mathbf{P}) \tilde{j}_{\ell''\sigma}(r, \mathbf{P}) \right) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) |R_{n\ell\sigma}(r, \mathbf{P})|^2 (Y_L(\hat{\mathbf{r}}, \mathbf{P}))^2 d\mathbf{r} \\
&= \sum_{L'L''L'''} C_{LLL'''} \sum_{\mathbf{P}} \int_{S_P} \frac{1}{n_\sigma(r, \mathbf{P})} \left(c_{L'j\sigma}^*(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'j\sigma}^*(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \times \\
&\quad \times \left(c_{L''j\sigma}(\mathbf{P}) \tilde{h}_{\ell''\sigma}(r, \mathbf{P}) + a_{L''j\sigma}(\mathbf{P}) \tilde{j}_{\ell''\sigma}(r, \mathbf{P}) \right) Y_{L''}(\hat{\mathbf{r}}, \mathbf{P}) |R_{n\ell\sigma}(r, \mathbf{P})|^2 Y_{L'''}(\hat{\mathbf{r}}, \mathbf{P}) d\mathbf{r} \\
&= \sum_{L'''} C_{LLL'''} \sum_{L'L''} C_{L'L''L'''} \sum_{\mathbf{P}} \times \quad (\text{B.16}) \\
&\quad \times \left[\begin{aligned} &c_{L'j\sigma}^*(\mathbf{P}) c_{L''j\sigma}(\mathbf{P}) \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{h}_{\ell''\sigma}(r, \mathbf{P}) d(r, \mathbf{P}) + \\ &+ c_{L'j\sigma}^*(\mathbf{P}) a_{L''j\sigma}(\mathbf{P}) \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell''\sigma}(r, \mathbf{P}) d(r, \mathbf{P}) + \\ &+ a_{L'j\sigma}^*(\mathbf{P}) c_{L''j\sigma}(\mathbf{P}) \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \tilde{h}_{\ell''\sigma}(r, \mathbf{P}) d(r, \mathbf{P}) + \\ &+ a_{L'j\sigma}^*(\mathbf{P}) a_{L''j\sigma}(\mathbf{P}) \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell''\sigma}(r, \mathbf{P}) d(r, \mathbf{P}) \end{aligned} \right].
\end{aligned}$$

Case 3: Both $i\sigma$ and $j\sigma$ correspond to valence states:

$$\begin{aligned}
\varphi_{i\sigma}(\mathbf{r}) &= \sum_L \left(c_{Li\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Li\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) Y_L(\hat{\mathbf{r}}, \mathbf{P}), \\
\varphi_{j\sigma}(\mathbf{r}) &= \sum_L \left(c_{Lj\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Lj\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) Y_L(\hat{\mathbf{r}}, \mathbf{P})
\end{aligned}$$

for \mathbf{r} inside S_P .

B.3 Calculation of the numbers $\bar{V}_{xj\sigma}^S$

To calculate

$$\bar{V}_{xj\sigma}^S = \Re \left\{ \sum_{\mathbf{P}} \int_{S_P} \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(r, \mathbf{P})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xi\sigma}(\mathbf{r}) d\mathbf{r} \right\} \quad (\text{B.18})$$

(cf. Eq. (6.122)) we use the already obtained inside S_P spherically averaged $(|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P})$ (see section B.1) and distinguish two cases for $j\sigma$.

Case 1: $j\sigma$ corresponds to a core state:

$$\varphi_{j\sigma}(\mathbf{r}) = R_{n'\ell'\sigma}(r, \mathbf{P}) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \quad (\text{B.19})$$

for \mathbf{r} inside S_P .

Using the orthonormality of the real valued spherical harmonics we have

$$\begin{aligned} \bar{V}_{xj\sigma}^S &= \Re \left\{ \sum_{\mathbf{P}} \int_{S_P} \frac{|R_{n'\ell'\sigma}(r, \mathbf{P})|^2}{n_\sigma(r, \mathbf{P})} (Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}))^2 \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d\mathbf{r} \right\} \\ &= \Re \left\{ \sum_{\mathbf{P}} \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} |R_{n'\ell'\sigma}(r, \mathbf{P})|^2 \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}) \right\}. \end{aligned} \quad (\text{B.20})$$

Case 2: $j\sigma$ corresponds to a valence state:

$$\varphi_{j\sigma}(\mathbf{r}) = \sum_L \left(c_{Lj\sigma}(\mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) + a_{Lj\sigma}(\mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \right) Y_L(\hat{\mathbf{r}}, \mathbf{P}). \quad (\text{B.21})$$

Starting immediately from the result in Eq. (6.122) we obtain

$$\bar{V}_{xj\sigma}^S = \Re \left\{ \sum_{\mathbf{P}} \sum_L \left[\begin{aligned} & \left(c_{Lj\sigma}^*(\mathbf{P}) c_{Lj\sigma}(\mathbf{P}) \times \right. \\ & \left. \times \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}) \right) + \\ & \left(c_{Lj\sigma}^*(\mathbf{P}) a_{Lj\sigma}(\mathbf{P}) + a_{Lj\sigma}^*(\mathbf{P}) c_{Lj\sigma}(\mathbf{P}) \right) \times \\ & \left. \times \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} \tilde{h}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}) \right) + \\ & \left(a_{Lj\sigma}^*(\mathbf{P}) a_{Lj\sigma}(\mathbf{P}) \times \right. \\ & \left. \times \int_0^{\bar{P}} \frac{(r, \mathbf{P})^2}{n_\sigma(r, \mathbf{P})} \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \tilde{j}_{\ell\sigma}(r, \mathbf{P}) \sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) d(r, \mathbf{P}) \right) \end{aligned} \right] \right\}. \quad (\text{B.22})$$

B.4 Calculation of the KLI exact exchange potentials $v_{x\sigma}^{\text{KLI}}(\mathbf{r})$

Starting from Eq. (6.123) we see that to obtain the inside S_P spherically averaged function $v_{x\sigma}^{\text{KLI}}(r, \mathbf{P})$ we need the spherical averages of the squares $|\varphi_{i\sigma}(\mathbf{r})|^2$.

When $i\sigma$ corresponds to a core state, i.e.,

$$\varphi_{i\sigma}(\mathbf{r}) = R_{n\ell\sigma}(r, \mathbf{P}) Y_L(\hat{\mathbf{r}}, \mathbf{P}) \quad (\text{B.23})$$

for \mathbf{r} inside S_P , this is due to the orthonormality of the real valued spherical harmonics given by

$$\frac{1}{4\pi} |R_{n\ell\sigma}(r, \mathbf{P})|^2; \quad (\text{B.24})$$

when $i\sigma$ corresponds to a valence state, i.e.,

$$\varphi_{i\sigma}(\mathbf{r}) = \sum_{L'} \left(c_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + a_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \right) Y_{L'}(\hat{\mathbf{r}}, \mathbf{P}) \quad (\text{B.25})$$

for \mathbf{r} inside S_P , it is for the same reason given by

$$\frac{1}{4\pi} \sum_{L'} \left[\begin{aligned} & c_{L'i\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ & + c_{L'i\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) + \\ & + a_{L'i\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) + \\ & + a_{L'i\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \end{aligned} \right]. \quad (\text{B.26})$$

Consequently we obtain

$$v_{x\sigma}^{\text{KLI}}(r, \mathbf{P}) = \Re \left\{ \frac{1}{n_\sigma(r, \mathbf{P})} \left[\sum_{i=1}^{N_\sigma} (|\varphi_{i\sigma}|^2 u_{xi\sigma})(r, \mathbf{P}) + \frac{1}{4\pi} \sum_{i=1}^{K_\sigma} |R_{n\ell\sigma}(r, \mathbf{P})|^2 \left(\bar{v}_{N_\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right] + \frac{1}{4\pi} \sum_{\ell'} \left[\begin{aligned} & \left(\tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \sum_{m_{\ell'}} \sum_{i=K_\sigma+1}^{N_\sigma} \times \right. \\ & \left. \times c_{L'i\sigma}^*(\mathbf{P}) c_{L'i\sigma}(\mathbf{P}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right) + \\ & \left(\tilde{h}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \sum_{m_{\ell'}} \sum_{i=K_\sigma+1}^{N_\sigma} \times \right. \\ & \left. \times 2\Re(c_{L'i\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P})) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right) + \\ & \left(\tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \tilde{j}_{\ell'\sigma}(r, \mathbf{P}) \sum_{m_{\ell'}} \sum_{i=K_\sigma+1}^{N_\sigma} \times \right. \\ & \left. \times a_{L'i\sigma}^*(\mathbf{P}) a_{L'i\sigma}(\mathbf{P}) \left(\bar{v}_{xi\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xi\sigma} + \bar{u}_{xi\sigma}^*) \right) \right) \end{aligned} \right] \right] \right\} \quad (\text{B.27})$$

where $\bar{v}_{xN_\sigma\sigma}^{\text{KLI}} - \frac{1}{2} (\bar{u}_{xN_\sigma\sigma} + \bar{u}_{xN_\sigma\sigma}^*) = 0$.

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Lebenslauf

18. August 1973	Geboren in Aschaffenburg als Tochter des Mess- und Regeltechnikers Alwin Bott und der Hausfrau Hilda Bott, geb. Baumgartl
1979–1983	Besuch der Grundschule der Volksschule Mainaschaff
1983–1992	Besuch des Friedrich-Dessauer-Gymnasiums Aschaffenburg
08. Juli 1992	Abitur
Oktober 1992 bis Oktober 1997	Studium der Mathematik mit Schwerpunkt Technik/Naturwissenschaften an der Technischen Hochschule Darmstadt
Oktober 1994 bis Juni 1995	Auslandsstudium am Trinity College Dublin
10. Oktober 1997	Diplom
Seit Oktober 1997	Beginn der Promotion bei Prof. Dr. P. C. Schmidt am Institut für Physikalische Chemie der Technischen Universität Darmstadt
Seit Dezember 1997	Wissenschaftliche Mitarbeiterin am Institut für Physikalische Chemie der Technischen Universität Darmstadt

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig und unter Verwendung nur der angegebenen Hilfsmittel angefertigt habe.

Bisher habe ich noch keinen Promotionsversuch unternommen.

Darmstadt, den 26. Oktober 1999